

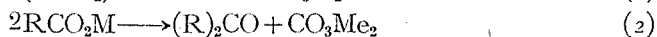
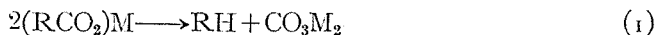
Studies on Ketones

By

Shintaro Araki

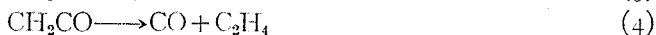
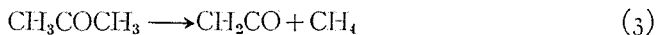
(Received November, 28th, 1932)

It is a well known fact¹ that fatty acids RCO_2H are transformed in the pyrolysis of their salts into hydrocarbons and ketones, and the formation of the former compounds (1) occurs mostly in their alkali salts and in the alkali earth salts the ketones predominate (2).



In the pyrolysis of a mixture of salts of two fatty acids, not only one mixed ketone as in the case of a mixture of potassium acetate and potassium isovalerate, observed by Williamson², but simple and mixed ketones such as ethyl ketone, isovaleron and ethyl isobutyl ketone are formed from a mixture of sodium propionate and isovalerate by dry distillation in an atmosphere of CO_2 ³.

The yield of these ketones by the reaction will depend partly upon the facility of any one of the two reactions (1) and (2) and also upon the stability of the resulting ketones towards heat. In the thermal decomposition of salts of fatty acids at about 600° the formation of ketones is, therefore, counted the main reaction and the product, obtained as tarry matter composed of the substances, and the stability of ketones towards heat, which was investigated in the case of the pyrolysis of acetone⁴ at about 500° (where the reactions occur), can be measured by the quantitative determination of CO in the gaseous product.



Carbon monoxide, which is presumed to be a decomposition product

1. Meyer & Jacobson, *Lehr. Org. Chem.*, Bd. 1, 586 (1907)
2. A. Williamson, *Ann.*, **81**, 86 (1852).
3. A. Genther & A. Loss, *Ibid.*, **202**, 327 (1880).
4. Schmidlin u. Bergmann, *Ber.*, **43**, 2821, 3517 (1910).

of ketone, according to the investigation by Boudonard,¹ is decomposed into CO_2 and C at about 350° , and cannot therefore be employed as an exact measure of the thermal decomposition of ketones.



The quantity both of CO and CO_2 in the gaseous product can be employed for this purpose, since in the pyrolysis of the salts CO_2 is originated in reaction (5) but not in the decomposition of the carbonate which is formed by reactions (1) and (2), as Riesenfeld² and Le Chatelier³ have independently reported that the decomposition of calcium carbonate occurs at least above 812° .

In the present communication, the writer's intention is to study the formation of ketones from various fatty acids, by which to measure indirectly the relative strength of affinity between the hydrocarbon radicals (R) and the carbonyl group; the yield of ketone in the tarry matter in the reaction products, as may easily be anticipated from the reactions shown above, can be employed for the measure of the affinity which can be checked by the quantitative determination of CO_2 and CO in the gas.

Acetic, propionic, butyric, isovaleric and palmitic acids are used for the purpose, their calcium salts being subjected to dry distillation at 600° with an apparatus constructed by the writer as will be seen in

Fig. 1.

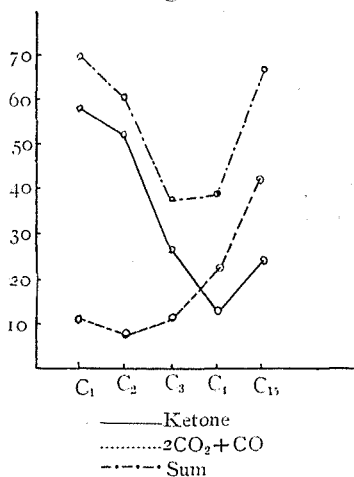
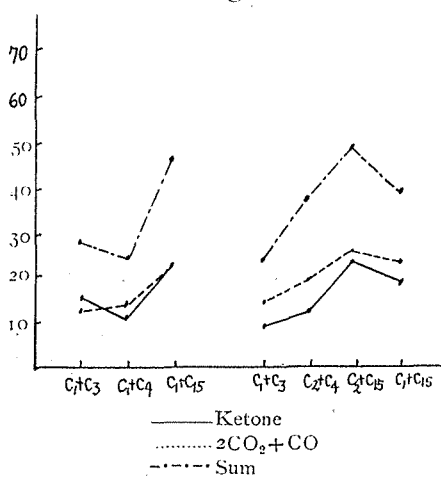


Fig. 2.



1. Boudonard, Z. Angew. Chem., **8**, 12 (1900).
2. Riesenfeld, Chemisches Zentralblatt, I, 996 (1910).
3. Le Chatelier, C. R., **102**, 1243 (1886).

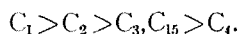
Fig. 1. The tarry product consists of ketone, hydrocarbon, water and acidic substances, and the gaseous product of carbon monoxide, carbon dioxide, saturated and unsaturated hydrocarbons and hydrogen. Of these products, the ketones in the tar and the carbon monoxide and carbon dioxide in the gas, were especially estimated in the present case, and the results obtained in the pyrolysis of single salts of organic acids are shown in Table I.

The yield of the tar usually increased in accordance with the molecular weight of acids except the acid C_4 , but the yield in mols per cent. of ketones resulting from 1 mol of each salt, as is indicated in Table II and Fig. 1 in which the yield is plotted by taking 100 times mol in the ordinate and the number of carbon atoms of the acids in abscissa, decreases inversely with the molecular weight of the acids,

Table I
(RCO_2)Ca=10 gms.

R=	C_1	C_2	C_3	C_4	C_{15}
Tar (gms.)	3.2	4.3	4.4	3.1	7.1
Gas (c.c.)	507	363	468	1378	1008
Coke (gms.)	6.2	5.4	4.8	4.3	1.8

showing the minimum yield in the acid C_4 . The radicals (C_n) are arranged in the strength of their affinity to the CO -group in the following order.



The order of the radicals arranged in relative strength of affinity, as we easily expected, is reciprocal to the order found from the quantity of CO_2 and CO generated :

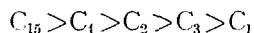


Table II

R=	C_1 (mol)	C_2 (mol)	C_3 (mol)	C_4 (mol)	C_{15} (mol)
Ketone	0.58	0.52	0.26	0.12	0.24
CO	0.07	0.05	0.06	0.19	0.25
CO_2	0.02	0.01	0.03	0.03	0.09
$CO+2CO_2$	0.11	0.08	0.11	0.26	0.42
Sum	0.69	0.60	0.37	0.38	0.66
Other ketones	0.19	0.17	0.39	0.20	0.22
Total ketones	0.88	0.77	0.76	0.58	0.88

The total yield of the ketone therefore, including other ketones of unknown nature, was found by calculation to be 88% in C_1 acid, 88% in C_{15} acid, 77% in C_2 acid, 76% in C_3 acid and 58% in C_4 acid.

The writer has extended his research on the formation of ketones from a single salt of the organic acids to a mixture in equimolecular weight of salts of two acids and the experimental results with regard to the formation of simple and mixed ketones are shown in Tables III, IV, V and VI.

Table III

R+R'	C_1+C_3	C_1+C_4	C_1+C_{15}
Tar (gms.)	3.6	3.4	6.2
Gas(c.c.)	546	750	459
Coke (gms.)	5.4	5.2	3.0

Table IV

R+R'	C_1+C_3	C_1+C_4	C_1+C_{15}
Ketone	C_1 0.06	C_1 0.06	C_1 0.10
	C_1, C_3 0.07	C_1, C_4 0.04	C_1, C_{15} 0.04
	C_3 0.02	C_4 0.01	C_{15} 0.08
Gas	CO 0.09	0.09	0.07
	CO ₂ 0.02	0.02	0.07
	CO+2CO ₂ 0.13	0.13	0.22
Sum	0.28	0.24	0.44
Other ketones	0.45	0.44	0.44
Total ketones	0.73	0.68	0.88

In the tables, (III, V), the yield of ketones, CO and CO₂ from 10 gms. of the mixed salts by dry distillation at 600° is shown, and the mol per cent. of these products is given in Tables IV and VI. Simple ketones are formed in the same relative amount in mol per cent. from

Table V

R+R'	C_2+C_3	C_2+C_4	C_2+C_{15}	C_3+C_{15}
Tar (gms.)	4.2	3.7	5.8	6.1
Gas (c.c.)	518	710	523	489
Coke (gms.)	5.1	4.9	2.9	3.2

Table VI

R+R'	C ₂ +C ₃ (mol)		C ₂ +C ₄ (mol)		C ₂ +C ₁₅ (mol)		C ₃ +C ₁₅ (m l)	
Ketone	C ₂	0.03	C ₂	0.06	C ₂	0.09	C ₃	0.04
	C ₂ , C ₃	0.05	C ₂ , C ₄	0.04	C ₂ , C ₁₅	0.06	C ₃ , C ₁₅	0.02
	C ₃	0.01	C ₄	0.02	C ₁₅	0.08	C ₁₅	0.08
Gas	CO	0.08		0.11		0.12		0.13
	CO ₂	0.03		0.04		0.07		0.05
	CO+2CO ₂	0.14		0.19		0.25		0.23
Sum		0.23		0.31		0.48		0.37
Other ketones		0.45		0.36		0.14		0.38
Total ketones		0.68		0.67		0.89		0.75

each two acids as in the case of pyrolysis of single acid; for example C₁=0.06 mol and C₃=0.02 mol in the mixed salts where C₁=0.58 and C₃=0.26 in the single salt.

Table VII

C ₁ +C ₃		C ₁ +C ₄		C ₁ +C ₁₅	
C ₁	0.06	C ₁	0.06	C ₁	0.10
C ₃	0.02	C ₄	0.01	C ₁₅	0.08

C ₂ +C ₃		C ₂ +C ₄		C ₂ +C ₁₅		C ₃ +C ₁₅	
C ₂	0.03	C ₂	0.06	C ₂	0.09	C ₃	0.04
C ₃	0.01	C ₄	0.02	C ₁₅	0.08	C ₁₅	0.08

C ₁	C ₂	C ₃	C ₄	C ₁₅
0.58	0.52	0.36	0.12	0.24

The yield of mixed ketones can be supposed to depend upon the relative strength of affinity of two radicals of the molecule to the CO-group, and in fact, as may be seen from the experimental results shown in Fig. 3, the ketones containing radicals of similar affinity formed in greater amount than that of radicals of different affinities, namely the decomposed ketones shown in the amount of CO₂ and CO in gaseous product, are in the order

$$C_2, C_4 > C_2, C_{15} > C_2, C_3 > C_3, C_{15},$$

$$C_1, C_3 > C_1, C_4 > C_1, C_{15}.$$

Fig. 3.

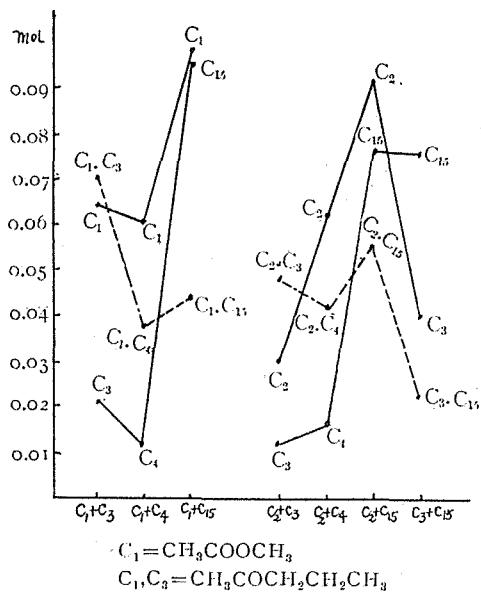
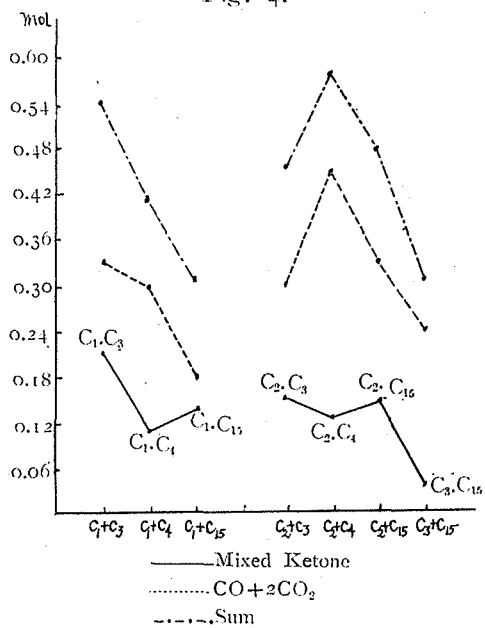


Fig. 4.



Experimental Part

In the experiments, acetic, propionic, butyric, isovaleric and palmitic acids were used after being purified, the first four being obtained by distillation from commodities and the last one being obtained by the writer from Haze kernel oil.¹

The calcium salts were made by neutralising the acids with calcium carbonate and were purified by extracting with alcohol some free acid mixed in them.

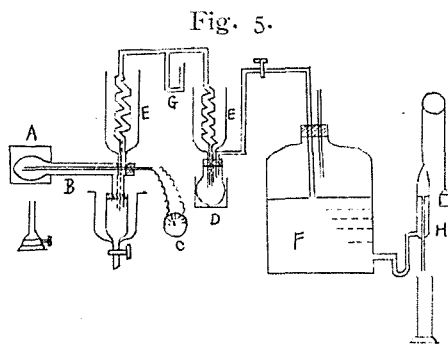


Fig. 5.
 A Distillation Chamber E Cooler
 B Distillation Flask F Gas Holder
 C Thermo-couple G Manometer
 D Receiver

10 grams of the sample were placed in a hard glass flask of about 40 c.c. with a long side tube, maintained at 600°C. in a closed square chamber 12 cms. 8 cms. 6 cms. made of gypsum and asbestos which was previously heated to about 620°C. with a coal gas flame.

The temperature in the reaction flask was measured with a thermo-couple inserted in it, (Fig. 5), and was regulated by means of a gas flame so as to reach 600°C. within 10 minutes after the flask had been introduced into the chamber, and the reaction was usually completed about 30 minutes. Throughout all the experiments the reaction was made to proceed at atmospheric pressure by controlling and measuring the pressure by a manometer attached to the apparatus and filled with an acidic water solution.

The tar and gas formed by the decomposition of the salts were collected separately in a receiver and a gas holder. The tar, composed of ketones, hydrocarbons and some quantity of acidic substances, was neutralised with CaCO_3 after being dehydrated with calcium chloride, and then fractionated carefully twice under the ordinary pressure to separate the required ketone only. The ketones of lower molecular weight in the distillate were confirmed by their physical constants and by means of the iodoform test² or by making the oxime³ and the

1. S. Komatsu & S. Shōyama, *These Memoirs*, 11, 533 (1928).

2. Messenger, *J. Chem. Soc. Abst.*, 313 (1889).

3. Meyerinzh, *Ber.*, 10, 1940 (1877); P. Petrenko Kritschenko u. S. L. Kipanidze, *Ibid.*, 34, 1702 (1901).

higher ones, which were separated by extraction with ether, were confirmed by their constants after weighing.

The generated gas which was composed of carbon monoxide, carbon dioxide, hydrogen and hydrocarbons of lower molecular weight, was analysed with the apparatus of Bone and Wheeler.

I. Calcium Acetate

Fig. 6.

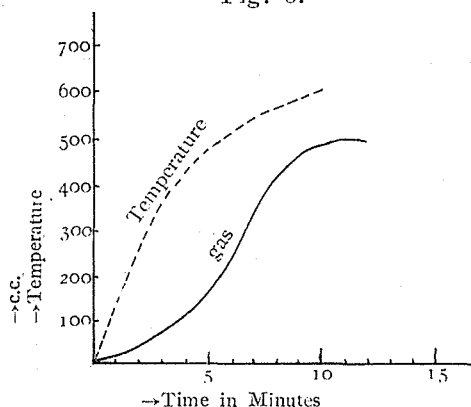


Table VIII

	Yield	
	obs.	calc.
Tar (gms.)	3.2	3.7
Gas (c. c.)	528	
Coke (gms.)	6.2	6.3

At about 130° , water was distilled out and then followed acetone at about 180° . The decomposition of the salt, as may be seen in Fig. 6, is vigorous at about 400° and was completed when the temperature had reached 580° ; the reaction products are shown in Table VIII. The actual yield of tar or acetone and coke from 10 gms. of the salt or CaCO_3 was compared with that calculated by the equation $(\text{CH}_3\text{CO}_2)_2\text{Ca} = (\text{CH}_3)_2\text{CO} + \text{CaCO}_3$.

Table IX

Fraction	B. p.	Yield	%	d_4^{25}	n_D^{25}	Acetone yield	
						%	Mol
		10.2					
1	56° – 65°	7.5	74	0.798	1.363	90	0.58
2	65° – 95°	1.2	12	0.816	1.372		
3	95° – 102°	0.3	3				
4	Residue	0.1	0.1				
5	Water	1.0	10				

10 gms. of tar, $d_4^{25} = 0.856$; $n_D^{25} = 1.371$, were fractionated into 5 fractions with the properties shown in the Table IX. Fraction 1, B. p. $56^\circ - 65^\circ$, was determined as being composed of 70% acetone by means of the iodoform test and also by the physical constants of pure ketone $d_4^{25} = 0.7895$; $n_D^{25} = 1.3571$; and the ketone was confirmed by converting it into a semicarbazone;

M. p. $189^\circ - 190^\circ$, N = 36.3% ($C_4H_9N_3O$, N = 36.5%).

The composition of the gases was determined with regard to CH_4 , H_2 , C_2H_4 , CO and CO_2 .

Table X

Gas analysis					
	$C_n H_{2n}$	$C_n H_{2n+2} + H_2$	CO_2	CO	Total
Vol. %	15.3	59.7	5.6	19.4	100
c. c.	1276	4980	468	1618	8342
Mol			0.02	0.07	

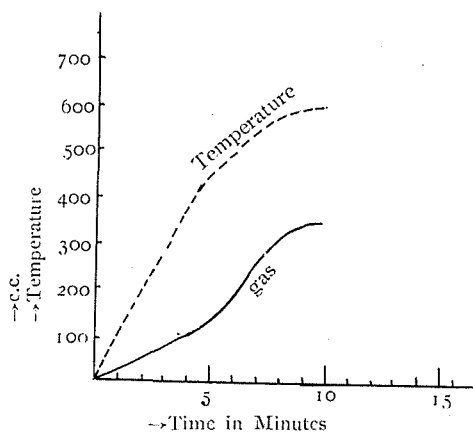
II. Calcium Propionate

10 gms. of the salt yield 4.3 gms. tar and 363 c.c. of gas; the behavior of the salt during the pyrolysis, which is similar to that of the acetate, is shown in Fig. 7.

Table XI

Material = 10gms.	Yield	
	obs.	calc.
Tar (gms.)	4.3	4.6
Gas (c.c.)	363	
Coke (gms.)	5.4	5.4

Fig. 7.



17.3 gms. of tar of a yellowish fluorescent oil ($d_4^{25} = 0.820$; $n_D^{25} = 1.390$) were fractionated into 5 fractions:

Table XII

Fraction	B. p.	Yield		d_4^{25}	n_D^{25}	Diethyl ketone yield	
		gms.	%			%	Mol
1	-100°	trace					
2	100°-107°	15.2	88	0.810	1.390	75.6	0.52
3	107°-224°	1.0	6	0.826	1.393		
4	Residue	0.5	3				
5	Water	0.5	3				

The second fraction, containing 88% of the tar, was distilled again and was ascertained to be diethylketone, B. p. 102°-103°, $d_4^{25}=0.8031$; $n_D^{25}=1.3905$, and yielding an oxime which gave on analysis N=13.9% ($C_6H_{11}ON$, N=13.85%). The gas was analysed with the following results.

Table XIII

	$C_{11}H_{24}$	$C_{11}H_{24+2}+H_2$	CO_2	CO	Total
Vol. %	16.2	61.5	4.5	17.8	100
c. c.	1094	4152	304	1201	6751
Mol		0.135	0.135	0.054	

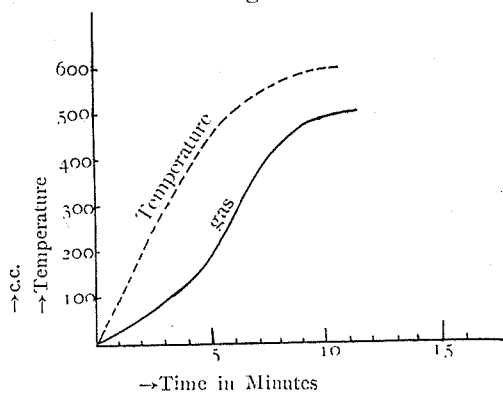
III. Calcium Butylate

The experimental results obtained by distillation of 10 gms. of the salt are as follows:

Table XIV

	Yield	
	obs.	calc.
Tar (gms.)	4.4	4.7
Gas (c.c.)	468	
Coke (gms.)	4.8	5.3

Fig. 8.



The evolution of gas in the distillation is shown in Fig. 8. 11.4 gms. of the tar ($d_4^{25}=0.830$; $n_D^{25}=1.406$), thus obtained, were fractionated into 7 portions:

Table XV

Fraction	B. p.	Yield		d_4^{25}	n_D^{25}	$(C_3H_7)_2CO$	
		gms.	%			%	Mol
1	102°-107°	little					
2	107°-115°	1.2	11	0.819	1.391		
3	115°-130°	2.9	26	0.808	1.394		
4	130°-140°	3.1	28	0.813	1.403		
5	140°-150°	3.1	28	0.822	1.405	74	0.261
6	Residue	0.9	8	0.844	1.427		
7	Water	little					

The fifth fraction was calculated from its physical constants to consist of 74% of dipropyl ketone which was isolated by distillation, its physical constants being determined: B. p = 143°-144°; $d_4^{25}=0.8201$; $n_D^{25}=1.4120$. Its oxime,¹ a viscous oil, was also analysed: N=10.7% ($C_7H_{15}NO$, N=10.85%).

The results of analysis of the gas are as follows:

Table XVI

	$C_n H_{2n}$	$C_n H_{2n+2}+H_2$	CO_2	CO	Total
Vol. %	39.3	42.4	5.6	12.7	100
c. c.	3734	4256	561	1276	10024
Mol			0.025	0.057	

1. V. Meyer u. Warrington, Ber., 20, 501 (1881).

IV. Calcium Isovalerate

Fig. 9.

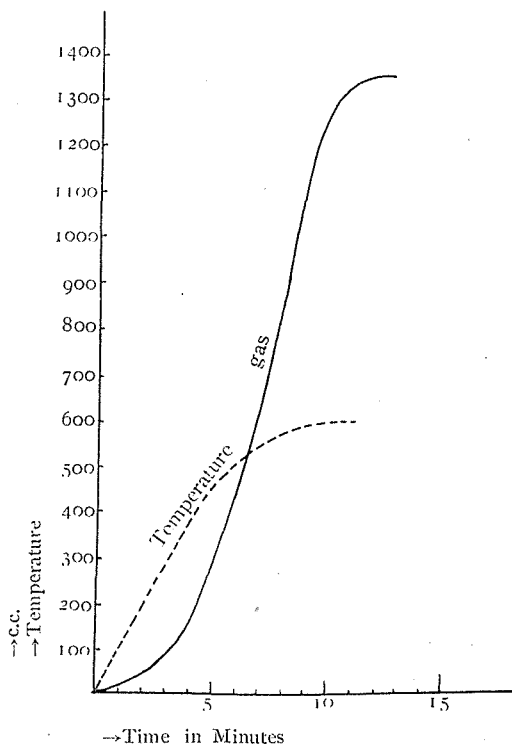


Table XVII

	Yield	
	obs.	calc.
Tar (gms.)	3.1	5.9
Gas (c.c.)	1378	
Coke (gms.)	4.3	4.1

The evolution of gas in the distillation is shown in Fig. 9. The reaction of dehydration was found to proceed at about 150° , and the formation of ketone was vigorous at about 500° . The reaction products obtained from 10 gms. of the salt are shown in Table XVII.

9.2 gms. of the tar ($d_4^{25} = 0.834$; $n_D^{25} = 1.420$)

were fractionated with the following results:

Table XVIII

Fraction	B. p.	Yield		d_4^{25}	n_D^{25}	$((\text{CH}_3)_2\text{CH} \cdot \text{CH}_2)_2\text{CO}$	
		gms.	%			%	Mol
1	$96^{\circ} - 120^{\circ}$	1.1	12	0.811	1.398		
2	$120^{\circ} - 160^{\circ}$	3.4	37	0.808	1.405		
3	$160^{\circ} - 170^{\circ}$	2.2	24	0.821	1.414	95	0.116
4	$170^{\circ} - 190^{\circ}$	1.1	12	0.835	1.427		
5	$190^{\circ} -$	1.2	13				
6	Water	0.2	2				

Isovalerone, which is the main constituent of the tar and which was isolated by repeated distillation of the third fraction, showed the

following constants: B. p. 164° — 166° ; $d_4^{25}=0.8279$; $n_D^{25}=1.4173$ and its oily oxime¹ gave on analysis $N=9.1$ ($C_9H_{19}NO$, $N=8.9\%$).

The other fractions indicate by their physical constants the occurrence of some other ketones.

The gas was analysed with the following results:

Table XIX

	$C_n H_{2n}$	$C_n H_{2n+2} + H_2$	CO_2	CO	Total
Vol. %	44.1	40.7	2.2	13.0	100
c. c.	14713	13570	727	330	29340
Mol			0.032	0.194	

V. Calcium Palmitate

Table XX

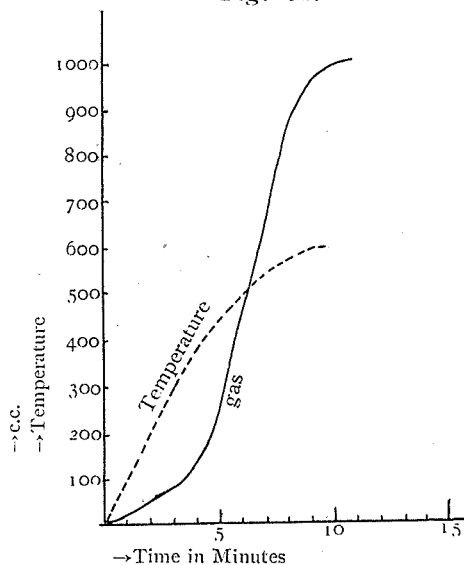
	Yield	
	obs.	calc.
Tar (gms.)	7.1	8.2
Gas (c.c.)	1008	
Coke (gms.)	1.8	1.8

The evolution of gas with time during the pyrolysis of the salt is shown in Fig. 10, and the results obtained from 10 gms. of the sample are shown in Table XX.

36 gms. of the tar were treated with ether to separate insoluble palmitone and the soluble part in the solvent was fractionated under 15 m.m.; the fraction with B. p. above 300° was again treated with cold ether to separate the palmitone from it.

For confirmation of palmitone thus obtained, its melting point (81° — 82°) and the nitrogen content of its oxime² (M. p. 57° — 58°), $N=3.0\%$ ($C_{31}H_{63}NO$, $N=3.0\%$) were determined.

Fig. 10.



1. Nef, Ann., **318**, 169 (1901); Skita, Ber., **41**, 2940 (1908).
 2. Kipping, J. Chem. Soc., **57**, 986 (1890).

Table XXI

Fraction	B. p.	Yield		d_4^{25}	n_D^{25}	$(C_{15}H_{31})_2CO$	
		gms.	%			%	Mol
1	48°—100°	2.9	12	0.775	1.427		
2	51°—150° (15m.m.)	5.0	20	0.803	1.439		
3	150°—200° (15m.m.)	3.5	14				
4	200°—250° (15m.m.)	3.9	16				
5	250°—280° (15m.m.)	2.3	9				
6	280°— (15m.m.)	1.6	6			35	0.019
7	Palmitone	5.6	23				0.217

Table XXII

	$C_n H_{2n}$	$C_n H_{2n+2} + H_2$	CO_2	CO	Total
Vol. %	35.9	50.8	3.5	9.8	100
c. c.	20240	27890	1925	5385	55440
Mol			0.086	0.25	

VI. A Mixture of Calcium Acetate and Calcium Butylate

An equimolecular mixture of the two salts above named was dissolved in water, evaporated to dryness and then subjected to pyrolysis as usual. The evolution of gas with time, as is shown in Fig. 11, reaches the maximum between 450° and 500°.

Fig. 11.

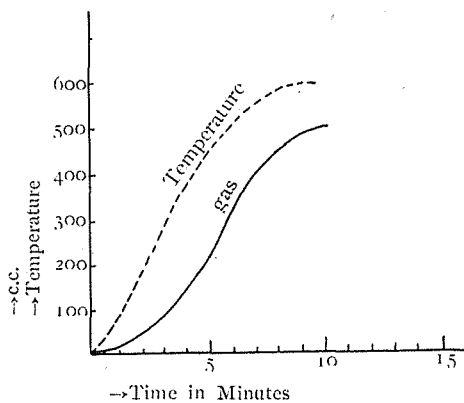


Table XXIII

	Yield	
	obs.	calc.
Tar (gms.)	3.6	4.6
Gas (c.c.)	547	
Coke (gn.s.)	5.4	5.4

The yield of tar and gas is shown in Table XXIII.

8.9 gms. of the tar $d_4^{25}=0.857$; $n_D^{25}=1.392$ were fractionated:

Table XXIV

Fraction	B. p.	Yield		d_4^{25}	n_D^{25}	Ketone	
		gms.	%			%	Mol
1	45°— 56°	trace					
2	56°— 65°	0.5	6.0	0.786	1.360	96	0.062
3	65°— 100°	2.8	33.3	0.806	1.371		
4	100°— 107°	0.9	10.7	0.808	1.383	86	0.068
5	107°— 140°	2.9	34.5	0.815	1.395		
6	140°— 150°	0.4	4.8	0.827	1.410	60	0.019
7	150°—	0.6	7.2	0.873	1.444		
8	Water	0.3	3.5				

Fractions 2, 4 and 6 in the Table were confirmed to be composed mostly of acetone, methyl propyl ketone and butyrene respectively from their physical constants, and the second ketone isolated from the 4th fraction by repeated distillation was confirmed to be so by its constants (B. p. 101°—102°; $d_4^{25}=0.8007$; $n_D^{25}=1.3888$) and by analysis of its oily oxime¹, N = 13.7% ($C_5H_{11}NO$, N = 13.9%).

Table XXV

	$C_n H_{2n}$	$C_n H_{2n+2} + H_2$	CO_2	CO	Total
Vol. %	41.5	34.5	4.4	19.6	100
c. c.	4222	3495	447	1990	10156
Mol			0.020	0.089	

VII. A Mixture of Calcium Acetate and Calcium Isovalerate

10 gms. of an equimolecular mixture of these two salts, prepared in a manner similar to the above were distilled at 600° and the yield of the products is shown in Table XXVI.

1. Beckmann, Ber., 20, 2581 (1887).

Fig. 13.

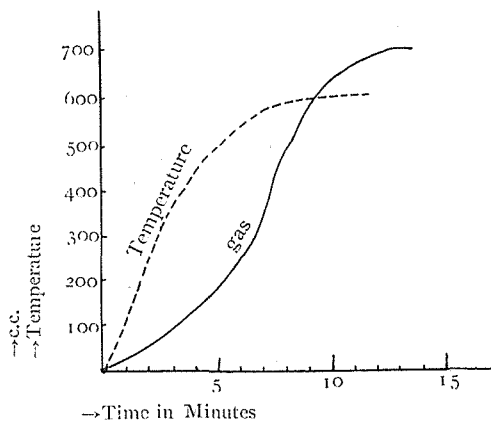


Table XXVI

	Yield	
	obs.	calc.
Tar (gms.)	3.4	4.9
Gas (c.c.)	790	
Coke (gms.)	5.2	5.1

9.3 gms. of the tar ($d_4^{25}=0.820$; $n_D^{25}=1.408$) were fractionated and acetone, methylisobutyl ketone and isovalerone were assumed from

Table XXVII

Fraction	B. p.	Yield		d_4^{25}	n_D^{25}	Ketone	
		gms.	%			%	Mol
1	48°—56°	trace					
2	56°—65°	0.6	7	0.802	1.363	85	0.06
3	65°—100°	1.7	18	0.795	1.369		
4	100°—115°	0.9	10	0.809	1.392		
5	115°—123°	1.5	16	0.804	1.397	35	0.04
6	123°—160°	2.9	31	0.812	1.407		
7	160°—170°	0.4	4	0.845	1.422	51	0.11
8	170°—	1.2	13				
9	Water	0.05	0.5				

their physical constants to be present in fractions 2, 5 and 7 respectively. The mixed ketone was isolated by repeated fractionation from the second fraction, and its constants (B. p. = 116°—117°; $d_4^{25}=0.8134$; $n_D^{25}=1.3971$) and the nitrogen content of its oily oxime, N = 12.1% ($C_6H_{13}NO$, N = 12.2%), were determined.

Table XXVIII

	$C_n H_{2n}$	$C_n H_{2n+2} + H_2$	CO_2	CO	Total
Vol. %	42.1	40.7	3.9	13.3	100
c. c.	6175	5971	578	1971	14694
Mol			0.023	0.088	

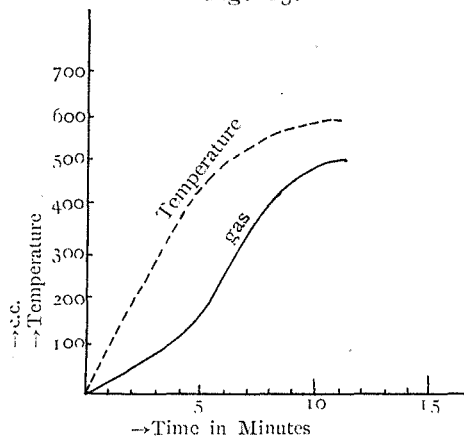
VIII. A Mixture of Calcium Acetate and Calcium Palmitate

10 gms. of an equimolecular mixture of the two salts were distilled, the gas-evolution with time and the reaction products being as shown in Fig. 13 and Table XXIX respectively.

Table XXIX

	Yield	
	obs.	calc.
Tar (gms.)	6.2	7.2
Gas (c.c.)	459	
Coke (gms.)	3.0	2.8

Fig. 13.



23.3 gms. of the tar were fractionated into 11 fractions and fractions 2, 7, 9 and 10 were observed to be composed mostly of acetone, methyl-

Table XXX

Fraction	B. p.	Yield		d_4^{25}	n_D^{25}	Ketone	
		gms.	%			%	Mol
1	45°-56°	0.4	1.8	0.721	1.364		
2	56°-65°	0.7	3.1	0.801	1.365	84	0.098
3	65°-100°	1.4	6.3	0.759	1.392		
4	100°-100° (15m.m.)	0.9	4.1	0.789	1.430		
5	100°-150° (15m.m.)	3.0	13.5	0.815	1.441		
6	150°-185° (15m.m.)	4.7	21.3				
7	185°-210° (15m.m.)	3.7	16.8			53	0.043
8	210°-300° (15m.m.)	2.9	13.1				
9	300°- (15m.m.)	0.9	4.1			29	0.006
10	Palmitone	3.4	15.4				0.075
11	Water	0.1	0.5				

pentadecyl ketone and palmitone respectively. From fraction 7, methyl-pentadecyl ketone was isolated by repeated fractionation. B. p. (225° — 227°) 110 m.m. M. p. 45° — 47° ; oxime, M. p. 29° — 30° , $N=13.2\%$ ($C_{17}H_{35}NO$, $N=13.1\%$).

Table XXXI

	$C_{11}H_{24}$	$C_{11}H_{20+2} + H_2$	CO_2	CO	Total
Vol. %	31	49	10	10	100
c. c.	5037	7961	1635	1635	16268
Mol			0.073	0.073	

IX. A Mixture of Calcium Propionate and Calcium Butylate

10 gms. of an equimolecular mixture of the two salts were distilled with the following results:

Fig. 14.

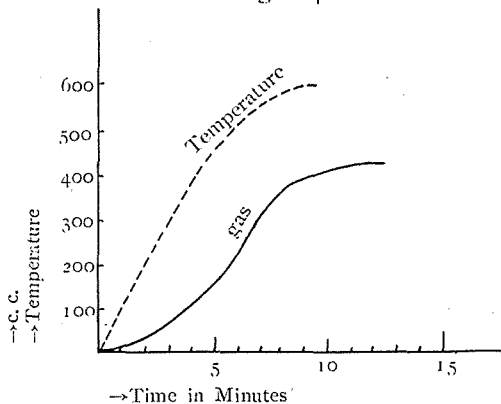


Table XXXII

	Yield	
	obs.	calc.
Tar (gms.)	4.4	5.0
Gas (c.c.)	518	
Coke (gms.)	5.1	5.0

11.4 gms. of the tar, $d_4^{25}=0.818$; $n_D^{25}=1.399$, were fractionated:

Table XXXIII

Fraction	B. p.	Yield		d_4^{25}	n_D^{25}	Ketone	
		gms.	%			%	Mol
1	70° — 100°	trace					
2	100° — 107°	0.9	8.0	0.811	1.387	36.1	0.030
3	107° — 120°	4.3	38.5	0.804	1.393		
4	120° — 128°	2.9	25.6	0.812	1.395	21.0	0.048
5	128° — 141°	1.6	14.6	0.823	1.401		
6	141° — 150°	0.8	7.1	0.815	1.407	22.2	0.012
7	150° —	6.2					
8	Water	trace					

Fractions 2, 4 and 6 were assumed from their physical constants to be composed mostly of diethyl ketone, ethylpropyl ketone and dipropyl ketone respectively. The mixed ketone with the constants B. p. = 123°—124°; $d_4^{25} = 0.9096$; $n_D^{25} = 1.3975$, was isolated by repeated fractionation of fraction 4 and its oily oxime was analysed: N = 13.2% ($C_6H_{13}NO$, N = 13.1%).

Table XXXIV

	$C_{11}H_{21}$	$C_{11}H_{21+2} + H_2$	CO_2	CO	Total
Vol. %	27.8	49.3	6.3	16.6	100
c. c.	2876	5114	652	1718	10360
Mol			0.029	0.077	

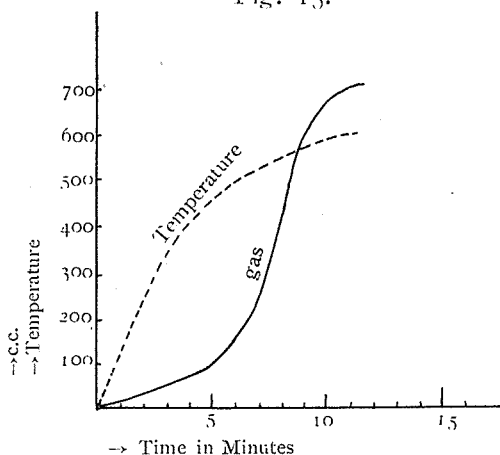
X. A Mixture of Calcium Propionate and Calcium Isovaleriate

10 gms. of an equimolecular mixture of the two salts were distilled with the following results:

Table XXXV

	Yield	
	obs.	calc.
Tar (gms.)	3.9	5.3
Gas (c.c.)	710	
Coke (gms.)	4.9	4.7

Fig. 15.



14.9 gms. of the tar, $d_4^{25} = 0.813$; $n_D^{25} = 1.411$, thus obtained, were fractionated.

Fractions 2, 4 and 6 are assumed from the physical constants to be composed mostly of diethyl ketone, ethylisobutyl ketone and isovalerone respectively, and ethylisobutyl ketone was confirmed to occur in the fraction 4 after being isolated by repeated distillation, the

following constants being determined; B. p. = 135° – 137° ; $d_4^{25} = 0.8123$
 $n_D^{25} = 1.4130$. Its semicarbozone¹ (M. p. 141° – 142°) was analysed.

Sample 0.0722 gms. N = 15.2 c.c. (16.8° , 762 m.m.) N = 24.4%
 ($C_8H_{17}N_3O$, N = 24.6%).

Table XXXVI

Fraction	B. p.	Yield		d_4^{25}	n_D^{25}	Ketone	
		gms.	%			%	Mol
1	65° – 100°	0.1	0.7	0.811	1.387		
2	100° – 107°	1.3	9.2	0.812	1.391	70	0.062
3	107° – 132°	6.3	44.7	0.812	1.398		
4	132° – 145°	2.0	14.2	0.816	1.406	43.6	0.042
5	145° – 160°	2.2	15.6	0.818	1.412		
6	160° – 170°	0.8	5.7	0.833	1.420	59.0	0.021
7	170° – 190°	0.5	3.6	0.849	1.433		
8	190° –	0.9	6.4				
9	Water	trace					

Table XXXVII

	$C_n H_{2n}$	$C_n H_{2n+2} + H_2$	CO_2	CO	Total
Vol. %	38.2	41.7	4.8	15.3	100
c. c.	6213	6780	782	2489	16264
Mol			0.035	0.111	

XI. A Mixture of Calcium Propionate and Calcium Palmitate

10 gms. of an equimolecular mixture of the two salts were distilled, and the results of the experiment are shown in Fig. 16 and Table XXXVIII.

Fig. 16.

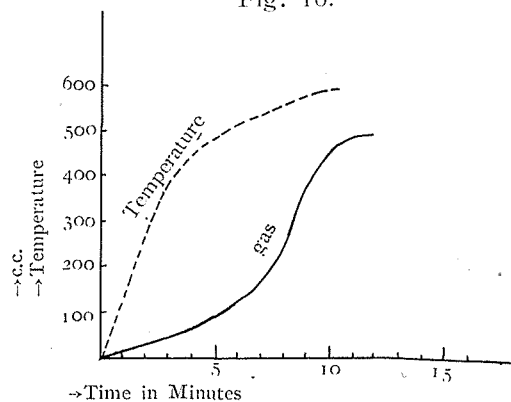


Table XXXVIII

	Yield	
	obs.	ca'c.
Tar (gms.)	6.1	7.3
Gas (c.c.)	523	
Coke (gms.)	2.9	2.7

1. Dilthey, Loc. cit.

26 gms. of the tar were fractionated into 10 portions:

Table XXXIX

Fr. ction	B. p.	Yield		d_4^{25}	n_D^{25}	Ketone	
		gms.	%			%	Mol
1	50°—100°	2.3	8.8	0.748	1.393		
2	100°—107°	2.4	9.2	0.791	1.399	38	0.091
3	107°—130°	0.6	2.3	0.802	1.405		
4	130°—150° (11m.m.)	4.8	18.4				
5	150°—195° (11m.m.)	6.0	23.0				
6	195°—202° (11m.m.)	2.5	9.6			73	0.059
7	202°—250° (11m.m.)	1.9	7.3				
8	250°—300° (11m.m.)	0.6	2.3				
9	300°— (11m.m.)	0.8	0.3				
10	Palm tone	4.2	16.1				0.080

Fractions 2, 6 and 10 were assumed from their physical constants to be composed mostly of diethyl ketone, ethyl pentadecyl ketone and palmitone respectively. Ethylpentadecyl ketone was identified to be so by determination of the constants B. p. = 197°—199° (11 m. m), M. p. 49°—50°, and analysis of its oxime²; M. p. 42°, N = 5.1% (C₁₈H₃₇NO, N = 5.0%) which was isolated from fraction 6 by fractional distillation.

Table XI.

	C _n H _{2n}	C _n H _{2n+2} + H ₂	CO ₂	CO	Total
Vol. %	32.5	46.0	17.8	13.7	100
c. c.	6255	8869*	1509	2612	19245
Mol		0.067	0.117		

1. J. Bertrand, *Chemisches Zentralblatt*, II, 289 (1896).
2. J. Bertrand, ditto.

XII. A Mixture of Calcium Butylate and Calcium Palmitate

10 gms. of an equimolecular mixture of the two salts were distilled with the following results.

Fig. 17.

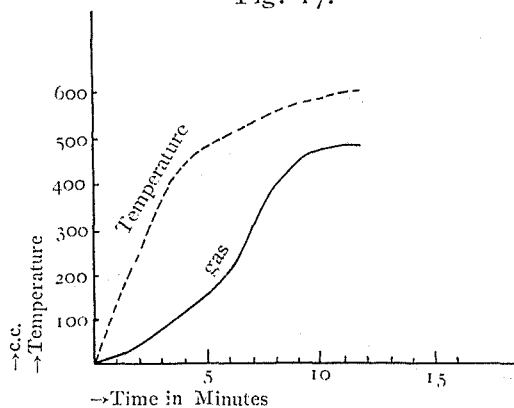


Table XII

	Yield	
	obs.	calc.
Tar (gms.)	6.4	6.8
Gas (c.c.)	489	
Coke (gms.)	3.2	3.2

22.2 gms. of the tar were fractionated and the yield and physical constants of the fractions are as follows:

Table XIII

Fraction	B. p.	Yield		d_4^{27}	n_D^{27}	Ketone	
		gms.	%			%	Mol
1	50°—140°	1.1	5.0	0.792	1.405		
2	140°—150°	0.9	4.1	0.823	1.412	44	0.040
3	60°—150° (15m.m.)	5.5	24.8	0.797	1.425		
4	150°—205° (15m.m.)	7.2	32.4	0.842	1.440		
5	205°—220° (15m.m.)	1.7	7.6			33.4	0.022
6	220°—280° (15m.m.)	1.9	8.5				
7	280°— (15m.m.)	0.9	4.1			18	0.004
8	Palmitone	3.0	13.5				0.073
9	Water	little					

Fractions 2, 5, 7 and 8 were assumed from their physical constants to be composed of dipropyl ketone, propylpentadecyl ketone and palmitone respectively, and the mixed ketone which was isolated from

fraction 5 was identified by determination of its constants, B. p. = $211^{\circ}-213^{\circ}$ (11 m.m.); M. p. = $47^{\circ}-48^{\circ}$; and analysis of its oxime (M. p. 24°) N = 4.7%, ($C_{19}H_{30}NO$; N = 4.7%).

Table XLIII

	$C_{11}H_{22}$	$C_{11}H_{22+2} + H_2$	CO_2	CO	Total
Vol. %	24.9	53.2	6.5	15.4	100
c. c.	4651	9938	1214	2877	18680
Mol			0.054	0.126	

In conclusion, the writer wishes to express his hearty thanks to Professor Shigeru Komatsu, at whose suggestion this work was undertaken, for his kind guidance.

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