

Absolute Rate Constants for the Reactions of O(³P) Atoms with Methyl Formate and Acetaldehyde

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Absolute rate constants for the reactions of ground state oxygen atoms with methyl formate and acetaldehyde have been determined at room temperature by means of a discharge-flow method combined with a time-of-flight mass spectrometer. The obtained values for methyl formate and acetaldehyde at 25°C are $(5.6 \pm 1.1) \times 10^9$ cm³ mole⁻¹ sec⁻¹ and $(2.9 \pm 0.4) \times 10^{11}$ cm³ mole⁻¹ sec⁻¹, respectively. These values are discussed in a correlation with the bond dissociation energy of C-H bond where the hydrogen abstraction will occur.

KEY WORDS : Reaction Kinetics/ Methyl Formate/ Acetaldehyde/ Bond Energy Correlation/

INTRODUCTION

The primary step in the reactions of the ground state oxygen atoms with alkanes, alcohols, aldehydes and ethers has been usually assumed to be the abstraction of a hydrogen atom. In our previous works on the reaction of oxygen atoms with dimethyl ether,^{1,2)} it has been shown that the observed reaction products could be explained as a result of the hydrogen abstraction by oxygen atoms. When the principal process in the primary reactions is assumed to be such hydrogen abstraction, it is expected that the rate constants or the activation energies will correlate with the bond dissociation energies of C-H bond where the reaction will occur. Huie and Herron³⁾ have attempted to correlate the activation energies in the reactions of oxygen atoms with some selected alkanes and oxygen-containing molecules with the bond dissociation energies, but they failed to find the linear relationship.

Singleton, Irwin and Cvetanović⁴⁾ have discussed the trend in the aldehydic C-H bond dissociation energies of some aldehydes in relation to the activation energies for the reactions of oxygen atoms with aldehydes or the C-H vibrational frequencies.

In the kinetic study of the reaction of iodine atoms with methyl formate, Solly and Benson⁵⁾ have obtained the C-H bond energy of 92.7 kcal/mole of the CHO group in methyl formate which is larger than that in formaldehyde (87.5 kcal/mole) or acetaldehyde (87.1 kcal/mole), and they have also suggested that the C-H bond of CH₃O group was much stronger (>100 kcal/mole) than that in dimethyl ether (93.3 kcal/mole).

On the basis of such consideration that the reaction rates must be closely related with the bond dissociation energies, the rate of abstraction by oxygen atoms from the CHO group in methyl formate is expected to differ from that in acetaldehyde. In this

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work, the determination of the rate constants for the reactions of oxygen atoms with methyl formate and acetaldehyde was attempted.

EXPERIMENTAL

Determination of the rate constants was made by means of a usual discharge-flow method combined with a mass spectrometer at room temperature. The apparatus and experimental technique are essentially identical with those used in our earlier work.²⁾

Ground state oxygen atoms were generated by a electrodeless discharge (2450 MHz) to the He-O₂ gas stream (containing 5~10% of O₂). In the case of the reaction with acetaldehyde, oxygen atoms produced by NO titration (reaction of N+NO→N₂+O) were also used in some runs for the comparison with the O₂ discharge system.

The absolute concentration of oxygen atoms was determined by NO₂ titration, *i. e.* a large excess of NO₂ was added to the oxygen atom-containing gas stream in the reaction zone. The amount of NO₂ consumed by the reaction of O+NO₂→NO+O₂ was measured by means of a time-of-flight mass spectrometer. The flow rate of NO₂ was corrected for the equilibrium of N₂O₄⇌2 NO₂.

Methyl formate or acetaldehyde was added to the gas stream containing oxygen atoms from the movable inlet downstream from the discharge zone. The consumption of the reactant was measured by means of a mass spectrometer, varying the distance between the sampling pinhole of the mass spectrometer and the inlet nozzle of the reactant. In the reaction of methyl formate, the intensity of molecular ion (*m/e*=60) was measured. While in case of acetaldehyde the intensity of (M-1)⁺ ion (*m/e*=43) was measured as the mass number of *m/e*=44 from the molecular ion of acetaldehyde overlapped to that from the ion of CO₂ produced.

The rate constant was obtained from the rate equation

$$\ln \frac{[M]_0}{[M]} = \int_0^t k[O] dt = k[O]t \quad (1)$$

under the pseudo-first order conditions ($[O]_0 \gg [M]_0$), where $[M]_0$ and $[M]$ refer to the initial concentration of the reactant and final one at a given reaction time, respectively. Reaction time t is a mean volumetric residence time (l/v), where l is a distance between the sampling pinhole of mass spectrometer and the reactant inlet nozzle, and v is a mean flow velocity of gas in the reaction zone.

Under the conditions that oxygen atoms exist in a large excess, the reactant has to be consumed predominantly by oxygen atoms, then the rate constant obtained from Eq. (1) is equal to that of the primary step, $O+M \xrightarrow{k} \text{products}$.

He (99.9999%) was obtained from Nihon Sanso Co. O₂ (99.95%) and N₂ (99.995%) were obtained from Takachiho Co. These gases were dried by passing through P₂O₅. Methyl formate (Nakarai Chemicals Co.) was purified by a preparative gas chromatography (with Porapak Q-S column). Acetaldehyde (E. Merck, 99%) was purified by repeating a bulb-to-bulb distillation until no impurities could be detected by gas chromatography. Both reactants were diluted (5% in He) and stored in large gas reservoirs at 80 Torr to keep the flow rate constant through an experimental run.

The time-of flight mass spectrometer Model 12-101S of Hokushin Electric Co. was used, and the microwave power system (2450 MHz, 200 W) was supplied by Itoh MW Co.

RESULTS AND DISCUSSION

1) Determination of the rate constant for the reaction of $\text{O} + \text{HCOOCH}_3$

The consumption of methyl formate (referred to as MF in the following) by the reaction with oxygen atoms was measured in the conditions of total pressure of 1~2 Torr at room temperature ($25 \pm 2^\circ\text{C}$).

A typical plot is shown in Fig. 1. A mean concentration of atomic oxygen $[\text{O}]$

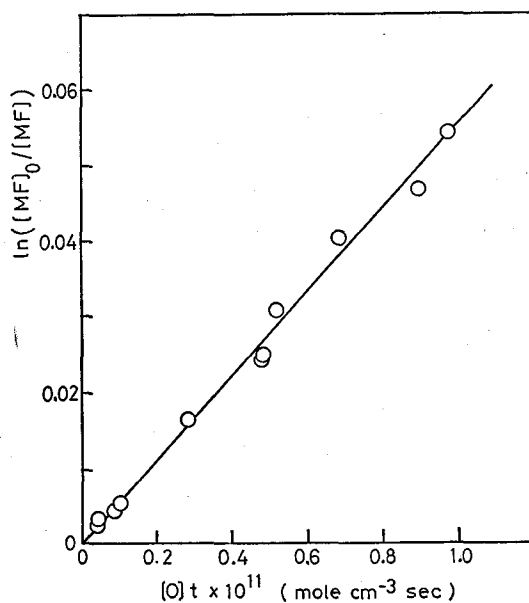


Fig. 1. A typical plot for the methyl formate consumption, in the conditions of $p=1.91$ Torr, flow velocity (v)=19.7 m/sec, $[\text{O}]_0=1.91 \times 10^{-9}$ mole/cm³, $[\text{MF}]_0=1.71 \times 10^{-11}$ mole/cm³, $T=25^\circ\text{C}$.

Table I. Rate constants for the reaction of $\text{O} + \text{HCOOCH}_3$.

p (Torr)	v (m/sec)	$[\text{O}]_0 \times 10^{10}$ (mole/cm ³)	$[\text{HCOOCH}_3]_0 \times 10^{10}$ (mole/cm ³)	$k \times 10^{-9}$ (cm ³ mole ⁻¹ sec ⁻¹)
2.01	14.7	26.3	0.221	5.51
2.00	14.7	23.8	0.0729	5.33
1.91	19.7	19.1	0.174	5.55
1.11	55.9	15.0	0.0596	6.21
1.62	23.7	8.22	0.198	5.74
1.57	32.1	7.89	0.131	5.41

Average 5.63 ± 0.29

through the reaction has to be used as shown in Eq. (I), while in the conditions of $[O]_0 \gg [MF]_0$, the decrease in the oxygen atom concentration by the reaction can be neglected and so $[O]_0$ was used approximately for $[O]$. In a fast flow system, a pressure decrease usually takes place along the gas stream, so that the initial concentration of oxygen atoms as well as the mean pressure in the reaction zone slightly changes with the distance l . Therefore, in Fig. 1 the product $([O] \times l)$ instead of reaction time t was used for the scale. Moreover, a clearance of 0.3 cm between the pinhole and the reactant inlet nozzle still existed even at a standard position of $l=0$ and small amounts of methyl formate were consumed in this region, then $\ln([M]_0/[M])$ was taken as to be 0 at $l=0$.

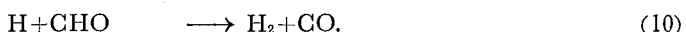
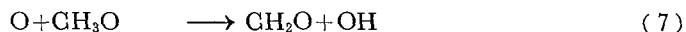
Several consumption rates of methyl formate were measured by varying the initial concentration of oxygen atoms, that of methyl formate, and the velocity of flowing gas, and the rate constants calculated from Eq. (I) are given in Table I.

Reaction products observed by means of the mass spectrometer were mainly CO_2 ($m/e=44$), and small amounts of CO ($m/e=28$) and H_2 ($m/e=2$). Although the formation of formaldehyde ($m/e=30$) was expected, no obvious increases in the intensity at $m/e=30$ was found under this condition.

From the observed products in this work, the following mechanism can be postulated, *i. e.* the primary process in the reaction of oxygen atoms with methyl formate seems to be the hydrogen abstraction from the formyl group similar to the case of iodine atoms as Solly and Benson suggested⁵⁾



which is followed by

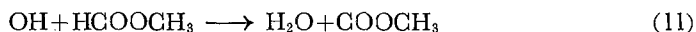


The activation energy for the reaction (3) is unknown. But the reaction has been assumed to be very fast on the basis of a low activation energy for the decomposition of the isomeric CH_3COO radical to CH_3 and CO_2 .^{5,6)} As the reactions between oxygen atoms and radicals are generally known to be fast, the reactions (5) and (7) are expected to be so and to have a rate constant comparable to $k_6(1 \times 10^{14} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1})$,^{7,8)} and this may be one reason for no detection of formaldehyde in this experiment. Using

the steady state approximation for the concentrations of radicals in the above reaction scheme, the ratio of formaldehyde to consumed methyl formate $[\text{CH}_2\text{O}]/\Delta[\text{MF}]$ can be estimated to be 0.26 at 20% decomposition of methyl formate, and 0.15 at 30% decomposition. Therefore, the detection of formaldehyde comes to be difficult under the conditions of a relatively low concentration of methyl formate such as in this work.

On the other hand, a large amount of CO_2 as observed may be due to the reaction (3), (5) and (9). According to these reactions, the yield of carbon dioxide $[\text{CO}_2]/\Delta[\text{MF}]$ has to take a value at least larger than 1.0, and a rough estimation gives 1.4 at 20% decomposition of methyl formate (using $k_9'/k_9=0.85$)⁹.

In this experiment, the formation of water was not distinct owing to the disturbance of the remaining water in the mass spectrometer.



Although the rate constant for the reaction (11) is unknown, the rate constants for the abstraction reactions by OH radicals have been known to be generally $10 \sim 10^2$ times larger than those for the reactions of oxygen atoms. Considering the rate constant for the consumption of methyl formate by oxygen atoms obtained above, therefore, k_{11} may be a value of $10^{10} \sim 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$. On the other hand, the reaction (4) is known to be very rapid ($k_4 = 3 \times 10^{13} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$)¹⁰, and then this becomes predominant under the conditions of $[\text{O}]_0 \gg [\text{MF}]_0$. A rough estimation for the concentration of OH radicals in this experimental condition gives $[\text{OH}]/[\text{O}] \leq 10^{-5}$. By assuming k_{11} to be $5 \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ as mentioned above, the yield of water $[\text{H}_2\text{O}]/\Delta[\text{MF}]$ can be estimated to be $\leq 10^{-3}$. This implies that in the rate equation for the consumption of methyl formate

$$-R_{\text{MF}} = k_1 \left(1 + \frac{k_{11}[\text{OH}]}{k_1[\text{O}]} \right) [\text{O}][\text{MF}],$$

$k_{11}[\text{OH}]/k_1[\text{O}]$ is less than 10^{-3} , and the rate constants for the consumption of methyl formate as given in Table I are approximately equal to k_1 . Now, for the primary reaction of $\text{O}(^3\text{P})$ with methyl formate,

$$k_1 = (5.6 \pm 1.1) \times 10^9 \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1} (25^\circ\text{C})$$

is obtained, where the error limits are estimated from the accuracy of the absolute oxygen atom concentration and the ratio $[\text{MF}]/[\text{MF}]_0$.

2) Determination of the rate constant for the reaction of $\text{O} + \text{CH}_3\text{CHO}$

The consumption rates of acetaldehyde were measured under the conditions similar to the case of methyl formate. A typical plot is shown in Fig. 2, and the obtained rate constants are given in Table II.

Major products observed by the mass spectrometer were $\text{CO}(m/e=28)$, $\text{CH}_2\text{O}(m/e=30)$, and $\text{CO}_2(m/e=44)$, although this mass number is the same as that from the molecular ion of acetaldehyde, the formation of CO_2 was surely confirmed by the difference between the change of $m/e=44$ and the change of $m/e=43$ from $(\text{M}-1)^+$ ion of acetaldehyde through the reaction). Small amounts of $\text{H}_2\text{O}(m/e=18)$ and $\text{H}_2(m/e=2)$

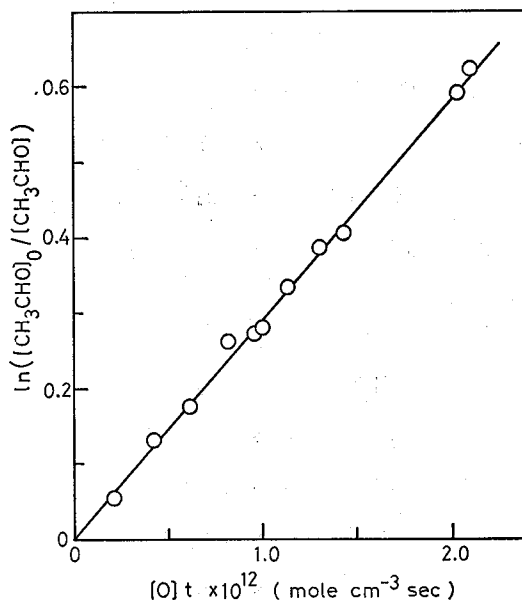


Fig. 2. A typical plot for the acetaldehyde consumption, in the conditions of $p=2.27$ Torr, Flow velocity (v)=14.4 m/sec, $[O]_0=3.62 \times 10^{-10}$ mole/cm³, $[CH_3CHO]_0=8.72 \times 10^{-12}$ mole/cm³, $T=25^\circ\text{C}$.

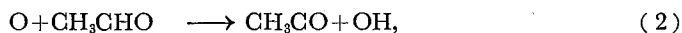
Table II. Rate constants for the reaction of $O+CH_3CHO$.

p (Torr)	v (m/sec)	$[O]_0 \times 10^{10}$ (mole/cm ³)	$[CH_3CHO]_0 \times 10^{10}$ (mole/cm ³)	$k \times 10^{-11}$ (cm ³ mole ⁻¹ sec ⁻¹)
1.59	21.7	9.00	0.171	3.06
1.62	21.3	4.21	0.177	3.03
2.27	14.4	3.62	0.0870	2.93
1.62	21.9	3.54	0.301	2.77
2.27	15.5	1.06 ^{a)}	0.0709	2.82
1.38	33.2	0.696 ^{a)}	0.0990	2.75
1.85	18.3	1.06 ^{a)}	0.159	2.97
				Average 2.90 ± 0.12

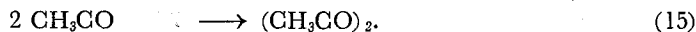
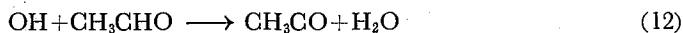
a) Oxygen atoms were generated by the reaction of $N+NO \rightarrow O+N_2$.

were also detected. Under the condition of a relatively high concentration of acetaldehyde, an additional increasing in the mass peaks of $m/e=42$, 58, and 86 was observed, these mass numbers corresponding to ketone, acetone, and biacetyl, respectively.

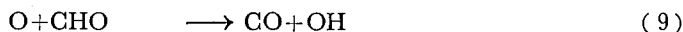
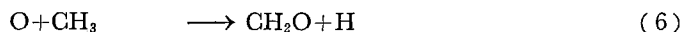
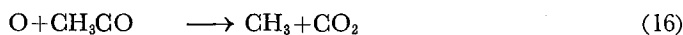
A confirmed mechanism has been established for the reaction of oxygen atoms with acetaldehyde. Avery and Cveticanovic,¹¹⁾ using oxygen atoms from the mercury photo-sensitized decomposition of N_2O , have postulated that the primary process involved the hydrogen abstraction reaction



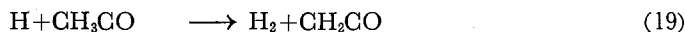
followed by



On the other hand, using a discharge-flow method similar to this work, Mack and Thrush¹²⁾ have proposed that the primary process (2) was followed by



The observed products in this work can be well interpreted by the mechanism proposed by Mack and Thrush, and the additional products (ketone, acetone, and bi-acetyl) suggest that at a higher acetaldehyde concentration the processes postulated by Avery and Cvetanović comes to contribute to the present reaction. The formation of ketene can be explained by the reaction (19) as suggested by McKnight, Niki, and Weinstock¹³⁾ for the reaction of hydrogen atoms with acetaldehyde.



Small amount of H_2 was found as the reaction product in the reaction of oxygen atoms with acetaldehyde, though it was not detected in the case of methyl formate. This can be attributed to the fast reaction of water formation (reaction (12); $k_{12} = 9.7 \times 10^{12} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$).¹⁴⁾ Under the present conditions, $[\text{OH}]/[\text{O}] \leq 1.4 \times 10^{-3}$ was estimated approximately, and this should lead to $[\text{H}_2\text{O}]/4[\text{CH}_3\text{CHO}] \leq 0.04$. The yield of water in the reaction of acetaldehyde is 40 times larger than that in the reaction of methyl formate shown above, and then the formation of water in the oxygen atom-acetaldehyde reaction is enough detectable. However, in the rate equation for the consumption of acetaldehyde

$$-R_{\text{CH}_3\text{CHO}} = k_2 \left(1 + \frac{k_{12}[\text{OH}]}{k_2[\text{O}]} \right) [\text{O}][\text{CH}_3\text{CHO}],$$

$k_{12}[\text{OH}]/k_2[\text{O}]$ is less than 0.04, and thus the rate constants for the consumption of acetaldehyde given in Table II are equal to k_2 within the experimental errors. Moreover,

as seen in Table II, there is no significant difference between the values of k in the O_2 discharge system and those in NO titration system in which O_2 is absent, and then it is concluded that O_2 has no significant effect on the consumption rate of acetaldehyde. Now, the rate constant for the primary process (reaction (2)) is obtained to be

$$k_2 = (2.9 \pm 0.4) \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1} (25^\circ\text{C}),$$

where the error limits are derived from the estimated accuracy of absolute oxygen atom concentration and the ratio of $[CH_3CHO]/[CH_3CHO]_0$. The obtained k_2 agrees well with the reported value of 2.88×10^{11} ,¹²⁾ or $2.59 \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$.⁴⁾

3) Correlation of the rate constants with the bond dissociation energies

The reaction of oxygen atoms with methyl formate has not been studied previously and no data are available for the comparison with the present k_1 . However, the obtained value of $5.6 \times 10^9 \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ is much lower than that for acetaldehyde ($k_2 = 2.9 \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$) or formaldehyde ($9 \times 10^{10} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$)⁹⁾. This low value is reasonable on the basis of a higher value (92.7 kcal/mole)⁵⁾ of the C-H bond energy in the CHO group of methyl formate compared with that of acetaldehyde (87.1 kcal/mole)¹⁵⁾ or formaldehyde (87.5 kcal/mole)¹⁶⁾. Therefore, the reaction (1) is expected to have a higher activation energy than those in the reactions of aldehydes. Although the temperature dependence of the reaction (1) could not be examined in this work, assuming that the pre-exponential factor of the reaction (1) is the same as that of the reaction of formaldehyde ($\log A = 12.57$)²⁰⁾, the activation energy of 3.9 kcal/mole can be estimated for the reaction (1). Assuming the upper and lower limits of $\log A_1$ to be 13.0 and 12.2, respectively, $E_1 = (3.9 \pm 0.5) \text{ kcal/mole}$ can be estimated, and a real value probably lies in this range.

In Table III, the bond dissociation energies of C-H bond where the abstraction reaction will occur, the room temperature rate constants, the activation energies, and

Table III. Bond dissociation energies and rate parameters

Molecule	$D(\text{C-H})$ (kcal/mole)	Ref.	$\log k^a$ at 25°C	E (kcal/mole)	$\log A^a$	Ref.
CH_3CHO^b	87.1	15	11.46			This work
			11.41	1.94	12.845	4
CH_2O	87.5	16	10.83	2.4	12.57	20
			10.95			9
CH_3OCH_3	93.3	17	10.49	2.85	12.70	21
			10.40	4.75	13.6	1
HCOOCH_3	92.7	5	9.75	(3.9) ^{c)}		This work
CH_3OH	95.5	18	9.92	3.05	12.16	22
CH_3COCH_3	98	19	8.48	5.7	12.63	23

a) Unit of k or A is $\text{cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$.

b) $\underline{\text{H}}$ refers to hydrogen atom abstracted by oxygen atom.

c) A estimated value assuming $\log A$ to be the same as that for formaldehyde.

the pre-exponential factors for the reaction of oxygen atoms with some oxygen-containing molecules are summarized. The pre-exponential factors for carbonyl compounds (aldehydes and acetone) are similar one another, but they are 3~5 times lower than those for alkanes (for example, $\log A=13.32$ for CH_4 , and 13.40 for C_2H_6 ²⁴⁾).

The values in Table III suggest that there is some correlation between the C-H bond dissociation energies and the activation energies or the room temperature rate constants, and this becomes to be clear by Fig. 3 where additional data of some alkanes and aldehydes are also included.

Concerning about the activation energies (Fig. 3a), a good linear relationship can

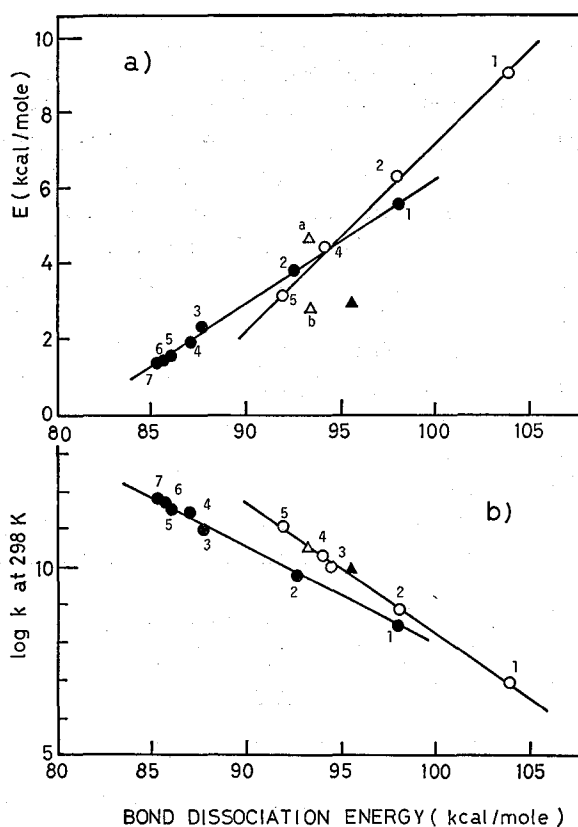


Fig. 3. Activation energy and rate constant as a function of bond dissociation energy.

a) activation energy vs. bond energy

b) room temperature rate constant vs. bond energy

○: alkanes, 1; CH_4 , 2; C_2H_6 , 3; C_3H_8 , 4; $n\text{-C}_4\text{H}_{10}$, 5; $(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)_2$ (rate data used are from Ref. 24, and bond energies are from Ref. 25, 26, 27)

△: CH_3OH , ▲: CH_3OCH_3 (data are from Table III, a; from Ref. 1, and b; from Ref. 21)

●: carbonyl compounds, 1; CH_3COCH_3 , 2; HCOOCH_3 , 3; CH_2O , 4; CH_3CHO , 5; $\text{C}_2\text{H}_5\text{CHO}$, 6; $n\text{-C}_3\text{H}_7\text{CHO}$, 7; $\text{iso-C}_3\text{H}_7\text{CHO}$ (data on 1, 2, 3 and 4 are from Table III, and data on 5, 6, 7 are from Ref. 4)

be seen for carbonyl compounds (closed circle), and another correlation is found for alkanes (open circle). The values for methanol and dimethyl ether (the data of dimethyl ether are somewhat scattered) seem to deviate from both correlations.

The room temperature rate constants for carbonyl compounds also correlate with the bond energies, and another correlation is found for alkanes (Fig. 3b). Those for methanol and dimethyl ether lie on the curve for alkanes.

With the Evans-Polanyi relationship, which Huie and Herron³¹ used to correlate activation energies (E) with the C-H bond dissociation energies ($D(\text{C-H})$),

$$E = \alpha [D(\text{C-H}) - C] \quad (\text{II})$$

and Arrhenius equation

$$\log k = \log A - E/\theta \quad (\theta = 2,303 RT),$$

the following expression can be led for the relation between the room temperature rate constants and the bond dissociation energies

$$\log k = (\log A + \alpha C/\theta) - (\alpha/\theta) D(\text{C-H}). \quad (\text{III})$$

Here, the coefficient α affects directly the slope in Eq. (III) and partly the intercept in Eq. (III). In case of carbonyl compounds, both α and C are lower than those in case of alkanes as seen in Fig. 3a, and the pre-exponential factors are also small as noted above. Therefore, the difference between the cases of carbonyls and alkanes would have become more distinct in the relations of the room temperature rate constants. Such difference in the correlations suggests that the activation energies or the room temperature rate constants are affected not only by the C-H bond energies, but by the other additional factors. It is probable that the nature of C-H bond in alkanes differ with that in the molecules which have an electronegative hetero atom such as oxygen. An electron density in the C-H bond adjacent to such electron attracting atoms may be decrease, then the C-H bond may become weak compared with the corresponding bond in alkanes. These are shown in Table IV. At the same time, assuming a linear activated complex in the transition state, the interaction of the attacking oxygen atom with the hydrogen atom may be also affected in a different way for the hetero

Table IV. Effect of hetero-atoms on the C-H bond dissociation energies.

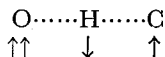
Molecule	$D(\text{C-H})$	(kcal/mole)
H-CH ₃	104 ^{a)}	
H-CH ₂ CH ₃	98 ^{a)}	
H-CH ₂ OH	95.5	
H-CH ₂ OCH ₃	93.3	
H-CCl ₃	90 ^{b)}	
H-CH=CH ₂	108 ^{a)}	
H-CH=O	87.5	

a) Values are from Ref. 25.

b) Value is from Ref. 26.

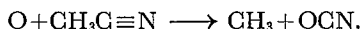
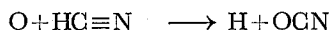
Unless otherwise noted, values are from Table III.

atom-containing molecules. Further, the repulsive interaction between the attacking oxygen atom and the carbon atom by the spin orientations such as



may also be the case.

Moreover, if other processes are involved besides abstraction reaction which proceeds by way of a linear activated complex, the activation energies are not directly affected by the C—H bond strengths, and α in Eq. (II) may become small. For example, it has been suggested that the primary process in the reactions of oxygen atoms with cyanides is not the hydrogen abstraction, but the addition reaction to the C $\equiv$ N bond^{28,29)}



In the reactions of carbonyl compounds, it may be possible that oxygen atoms interact with the π bond of carbonyl (>C=O) similar to C $\equiv$ N or C=C.

Consequently, it is concluded that these effects which are not involved in the reaction of alkanes would make the correlation in the case of carbonyl compounds differ from that in alkanes.

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