

(4) The rate of oxygen absorption is markedly affected by a variation in alkali concentration. Relative mean ionic activity ( $a_r$ ) of KOH in methanol was measured electrochemically. The plots of the rate ( $dV/dt$ ) of oxygen absorption against the relative activity ( $a_r$ ) as well as its square ( $a_r^2$ ) indicate that  $dV/dt$  is proportional linearly to  $a_r^2$ , but not to  $a_r$  itself. Since the activity of undissociated alkali is given by  $a_r^2/C$ , where  $C$  is a constant, it is possible to consider that the rate of oxygen absorption increases in the first order with the activity of undissociated alkali.

(5) If the reaction held in an aqueous methanolic solution (1:7 by volume), the rate was retarded to about one third. This probably due to the decrease in activity of undissociated alkali owing to better dissociation in an aqueous methanolic solution.

### 13. Activation of Methyl Group by Nitro Group. (VI)

#### A Possible Reaction Mechanism

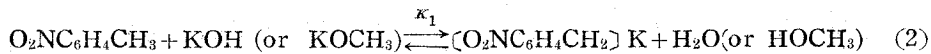
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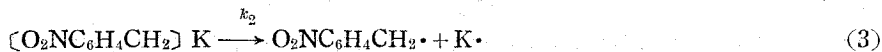
From the experimental results stated in the preceding paper, the following rate law is possible.

$$dV/dt = k_1 [p\text{-nitrotoluene}] [\text{undissociated alkali}] \quad (1)$$

where  $dV/dt$  is the rate of oxygen absorption and  $k_1$  is a rate constant. Considering the property as active methyl group in *p*-nitrotoluene, it is very reasonable to assume the following equilibrium;

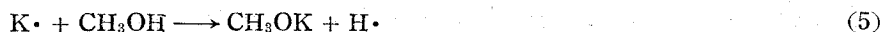


where  $K_1$  is an equilibrium constant. The formation of several oxidation products of methanol suggests a radical type decomposition of the salt, i. e.,

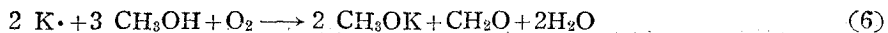


where  $k_2$  is a rate constant.

The nitrobenzyl radicals thus formed probably combine to give rise to dinitrodibenzyl, whereas the potassium radical or atom reacts with methanol to form potassium methylate and hydrogen.



It is probably this hydrogen that absorbs oxygen, i. e., hydrogen combines with oxygen to form peroxides such as  $\text{HO}_2\cdot$  and  $\text{H}_2\text{O}_2$  which react with methanol (formaldehyde) to give rise to formaldehyde (formic acid). Thus, overall reaction is probably expressed as follows.



Quantitative relation between the reactants and products expected from equation (6) is in good accord with our observation. Equation (1) can be derived from the assumption that reaction (2) determines the overall rate, but similar result is also derived from reaction (3). Therefore, it cannot be decided which is the rate determining step. However, according to our observation, *p*-nitrotoluene is somewhat soluble in aqueous alkali, and from the latter the nitrotoluene is reversibly recovered by adding mineral acid. This fact supports the assumption that equilibrium (2) is rapidly set up and the radical type decomposition of the salt, i. e., reaction (3) determines the rate.

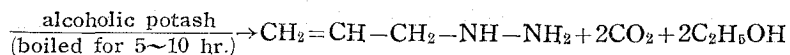
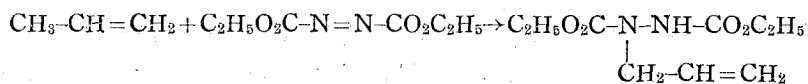
The authors are grateful to Professor Ryhei Oda for his suggestive discussion and encouragement in this work, to Professors Shinzo Okada and Shiro Yoshizawa and Mr. Fumio Hine, Department of Industrial Chemistry, Kyoto University, for their helpful discussions and laboratory experiments in the electrochemistry.

#### 14. Studies on the Reaction of Ethyl Azodicarboxylate and Ethyl Oleate

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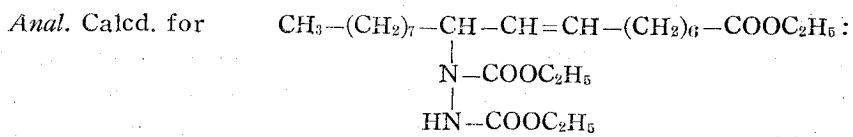
It has already been known that *N*-allylhydrazo-*N,N'*-dicarboxylic ester is produced when olefin is reacted with azodicarboxylic ester at room temperature and the product is saponified with alcoholic potash (E. Müller: *Z. angew. Chem.*, **63**, 18).



The authors have attempted this reaction with ethyl oleate. The azodicarboxylic ester was synthesized according to the method of *Org. Synth.* **82**, 58.

The results are summarised in the following:

(1) The reaction product from azodicarboxylic ester and oleic ethyl ester (yield; quantitative).



N, 5.77; Found: N, 5.45.