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Pressure-dependence of Alkyl Radical Reactions

By J. GROTEWOLD, E. A. LISSI, and M. G. NEUMANN

(*Departamento de Quimica Inorganica, Analitica y Quimica Fisica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Argentina*)

IN recent years there has been considerable interest in the pressure-dependence of combination reactions between alkyl radicals. However, most work has had a theoretical approach. Practically the only experimental investigations on which these theories could be tested are those of Kistiakowsky and Roberts,[1] and Dodd and Steacie[2] who studied the pressure-dependence of the combination of methyl radicals using acetone as radical source; and Toby and Weiss[3] who studied the same effect in photolysis of azomethane. Their results were not exact enough to allow theoretical calculations (*e.g.*, the calculation of s, number of degrees of freedom involved in the reaction). Brinton and Steacie[4] found that in the reaction between ethyl radicals there was a trend with pressure for the ratio $k_{\mathrm{abstr.}}/k^{\frac{1}{2}}_{\mathrm{comb.}}$, but they failed to observe a similar trend for $k_{\mathrm{dispr.}}/k_{\mathrm{comb.}}$. From this they concluded that the disproportionation reaction is also pressure-dependent.

We now report a study of the methyl–ethyl radical system. This work was undertaken in order to obtain significant data for (*a*) the evaluation of the parameter s for the combination reaction; and (*b*) to find whether there is a real third-body dependence for the disproportionation reaction.

A mixture of azomethane and azoethane was photolysed with a mercury arc lamp. The pressure was measured by expansion of small calibrated volumes of reactants into a 10-l. Pyrex cell. The system followed the well known set of reactions

$$CH_3 + CH_3 = C_2H_6 \quad .. \quad .. \quad (1)$$

$$CH_3 + C_2H_5 = C_3H_8 \quad .. \quad .. \quad (2)$$

$$CH_3 + C_2H_5 = CH_4 + C_2H_4 \quad .. \quad (3)$$

$$C_2H_5 + C_2H_5 = C_4H_{10} \quad .. \quad .. \quad (4)$$

$$C_2H_5 + C_2H_5 = C_2H_4 + C_2H_6 \quad .. \quad (5)$$

From the experimental data one can calculate the k_3/k_2 ratio and the cross-combination ratio k_2^2/k_1k_4, using

$$\frac{k_3}{k_2} = \frac{R_{C_2H_4(3)}}{R_{C_3H_8}} \qquad (I)$$

$$\frac{k_2^2}{k_1k_4} = \frac{R^2_{C_3H_8}}{R_{C_2H_6(1)}\,R_{C_4H_{10}}} \qquad (II)$$

The other reactions that could give contributions to the measured yields are the hydrogen abstraction reactions, and the unimolecular cleavage

$$CH_3N_2CH_3 = C_2H_6 + N_2 \quad .. \quad (6)$$

The former was seen to be negligible, after photolysing azoethane in the same conditions and observing equal yields of ethane and ethylene. From the results of Rebbert and Ausloos[5] it follows that reaction (6) is only important if a small fraction of the methyl radicals react to give ethane, which is not the case. Then, the cross-combination ratio can be calculated from

$$\frac{k_2^2}{k_1k_4} = \frac{R^2_{C_3H_8}}{(R_{C_2H_6} - 0{\cdot}125R_{C_4H_{10}})\,R_{C_4H_{10}}} \qquad \text{(III)}$$

The values obtained for pressures down to 0·08 Torr. are: for k_3/k_2 0·035 ± 0·004, and for the cross-combination ratio 4·00 ± 0·15. These values are in good agreement with previous determinations. Further, the cross-combination ratio is also in agreement with the values expected on a statistical basis.

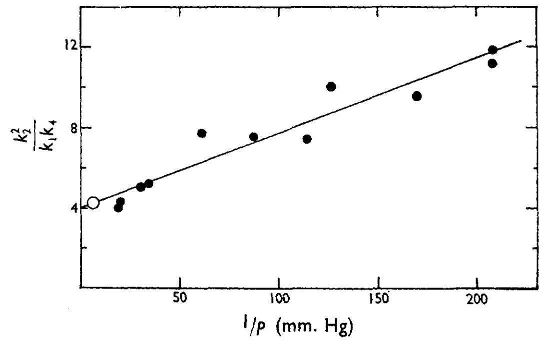

FIGURE. *Pressure-dependence or the cross-combination ratio assuming a simple Hinshelwood–Lindemann behaviour for the methyl radical combination at* 15° C. *The white point is the average of* 23 *high-pressure runs.*

An increase of the cross-combination ratio with decreasing pressure was found at pressures lower than 0·08 Torr. This was ascribed to reaction (1) being in the pressure-dependent region. In the Figure this dependence is shown assuming a simple Hinshelwood–Lindemann behaviour.

As shown by Slater,[6] the Rice–Rampsberger–Kassel theory predicts that

$$P_{\frac{1}{2}} \propto T^{s-\frac{1}{2}} \qquad \text{(IV)}$$

where $P_{\frac{1}{2}}$ is the pressure at which $k_{1\,\mathrm{exp.}}$ is one half of its value at high pressure, and s is the number of internal degrees of freedom which contribute to the reaction.

We tried to compare the result obtained in this paper with the values obtained by Kistiakowsky and Roberts, Dodd and Steacie, and Toby and Weiss, but this could not be done because their values did not show the trend expected according to Equation IV. This failure may be due to their systems involving hydrogen abstraction, which is supposed to have an appreciable heterogeneous contribution[7] even at 50° C. The results reported here also show that the fall-off region for ethyl–ethyl recombination must be far below the pressure reported by Brinton and Steacie.

From all this it can be concluded that the method of following pressure-dependence of radical reactions described here has some advantages over those reported previously, and on this basis we are performing similar studies at different temperatures using this method.

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