

The Rate Constant of the Methyl Radical Recombination Reaction

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qualitatively and preliminary work indicates that quantitative agreement may also be found.

Thus, if this explanation is correct it should be possible to arrange chemically inert gases in the order of the amount of free chlorine that is produced in the reaction discussed here or some other convenient product. The dividing line between those that cause reactions and those that do not could then be shifted arbitrarily by varying the acoustic intensity. Furthermore a study of a series of reactions that go with measurable speed at different temperatures should give further evidence for understanding the phenomena. There is an intensity threshold below which these reactions will not take place no matter what gas is present but little can be said about its value until the absolute value of the sound intensity is measured. It is hoped to publish a full report of this work in the near future.

¹ Weissler, Cooper, and Snyder, *J. Am. Chem. Soc.* **72**, 1769 (1950).

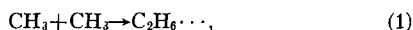
² These ideas were stimulated by a talk given in the Catholic University Physics Department by Richard R. Carhart, of the California Institute of Technology. His talk was taken from his Ph.D. thesis "Theory of viscous and thermal attenuation of sound by small spheres."

The Rate Constant of the Methyl Radical Recombination Reaction

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May 18, 1950

IT has proved possible to estimate the lifetime of methyl radicals in a static system and to compute the rate constant of the homogeneous second-order recombination reaction:



as follows: Mercury dimethyl was irradiated with a medium pressure mercury arc and provision was made for chopping the light beam with a rotating sector having a light to dark ratio of one.

The theory of the rotating sector has been worked out by Dickinson¹ for the case:



The equations cannot be solved readily for the case where the radicals $R\cdot$, formed in the primary process, disappear by both first- and second-order reactions, nor will the speed of light interruption have any effect on the rate of reaction (3) when it predominates, since it then is proportional to I_a . It is therefore necessary to have some means of determining the steady state concentration of $R\cdot$, which is proportional to I_a ¹. In the present case the formation of methane was used as a "pilot" reaction for this purpose.

It is possible to adjust the light intensity in such a way that the rate of ethane formation is arbitrarily large compared to the rate of methane formation.² Working in the range where $RC_2H_6/RCH_4 \approx 25$, the bulk of CH_3 radicals disappears by ethane formation. The formation of methane can be measured quite

accurately, however, and is proportional to the CH_3 steady state concentration.²

It was found that the experimentally obtained curve of $RCH_4/\bar{R}CH_4$ versus $\log \Delta t_1$ at 175° (where RCH_4 refers to methane formation under interrupted and $\bar{R}CH_4$ to that quantity under steady illumination and Δt_1 to the time of one light flash) follows the theoretical curve very well, leading to superposition when the mean lifetime is given the value 10 milliseconds at a (bimolecular rate of ethane formation of 3.6×10^{-11} mole/cc sec. This leads to a value of the rate constant of reaction (1) of 7×10^{13} (moles/cc)⁻¹ sec.⁻¹, at 175° .

The measurements are being extended to other substances yielding CH_3 radicals, and to higher temperature ranges in order to obtain the activation energy of reaction (1). Details of the work and the significance of the large value of k_1 and its apparent independence of pressure in the range of 5 to 100 mm³ will be discussed in full at a later time.

The author wishes to express his gratitude for many valuable suggestions and advice to Professor G. B. Kistiakowsky, and to the AEC which is supporting this work.

* AEC Postdoctoral Fellow 1949-50.

¹ W. A. Noyes, Jr. and P. A. Leighton, *The Photochemistry of Gases* (Reinhold Publishing Corporation, New York City, 1941), pp. 202-209.

² R. Gomer and W. A. Noyes, Jr., "The photochemistry of mercury dimethyl," *J. Am. Chem. Soc.* **71**, 3390 (1949).

³ R. Gomer and W. A. Noyes, Jr., "Photochemical studies. Ethylene oxide," *J. Am. Chem. Soc.* **72**, 106 (1950).

A Reply to H. S. Gutowsky and E. M. Peterson Regarding the Ozone Spectrum

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May 12, 1950

TO avoid unnecessary confusion regarding the ozone spectrum it appears desirable to point out that the analysis of the infra-red spectrum based on an acute angled molecular model proposed by Gutowsky and Peterson¹ appears to be completely excluded on at least two different grounds. (Incidentally the heading of columns 2 and 3 of their Table I appear to be interchanged.)

The spectrum of ozone was carefully examined in this laboratory at both room and dry ice temperatures. Some moderate changes were observed in the relative intensities of the band maxima, due to unequal narrowing of the bands at the low temperature, but the possibility is completely excluded that any of the seven bands under discussion is a difference band involving a lower excited level of 750 cm^{-1} or greater.

The acute angled model consequently fails to account for the band at 1110 cm^{-1} . In any case the large difference between the observed and predicted frequencies completely rules out the possibility that 1110 cm^{-1} is $\nu_1 - \nu_2$ of an acute angled molecule, and makes the alternative interpretation, $3\nu_3 - \nu_2$, most improbable.

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¹ H. S. Gutowsky and E. M. Peterson, *J. Chem. Phys.* **18**, 564 (1950).

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