

Theoretical Explanation of the Chemical Effects of Ultrasonics

Virginia Griffing

Citation: [The Journal of Chemical Physics](#) **18**, 997 (1950); doi: 10.1063/1.1747840

View online: <http://dx.doi.org/10.1063/1.1747840>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/18/7?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[A theoretical study of the chemical vapor deposition of \(100\) diamond: An explanation for the slow growth of the \(100\) surface](#)

J. Chem. Phys. **113**, 7582 (2000); 10.1063/1.1311976

[A physical explanation of the gyroscope effect](#)

Am. J. Phys. **45**, 1194 (1977); 10.1119/1.10698

[An Explanation of the dc Sumoto Effect](#)

J. Appl. Phys. **33**, 941 (1962); 10.1063/1.1777194

[The Chemical Effects of Ultrasonics](#)

J. Chem. Phys. **20**, 939 (1952); 10.1063/1.1700654

[Comment on ``Theoretical Explanation of the Chemical Effects of Ultrasonics''](#)

J. Chem. Phys. **18**, 1513 (1950); 10.1063/1.1747525



Now, any molecule within a distance θ of a surface element dS , and traveling towards it, will strike dS during one second.

Originate a spherical coordinate system at dS . The volume element

$$d\tau = r^2 \sin\theta d\theta d\varphi dr \quad (4)$$

will contain $C_a d\tau$ molecules (where C_a is the uniform concentration of solute) of which the fraction

$$(dS \cos\theta)/(4\pi r^2) \quad (5)$$

will strike dS during one second provided that

$$r \leq \theta. \quad (6)$$

Expression (5) is a statement of the isotropic distribution of velocity vectors. According to this formulation

$$\begin{aligned} \beta_a dS &= \frac{C_a dS}{4\pi} \int_0^\pi \int_0^{\pi/2} \int_0^{2\pi} \sin\theta \cos\theta d\varphi d\theta dr \\ &= \frac{3}{2} \frac{D}{\langle l^2 \rangle^{1/2}} C_a dS, \end{aligned} \quad (7)$$

or

$$\beta_a = \frac{3}{2} \frac{D}{|l|} C_a.$$

This value is accurate enough for use in the above-mentioned nucleation theory, especially since the rate of nucleation is dependent mostly upon an exponential factor, already evaluated, which does not contain β_a .

¹ H. Reiss, *J. Chem. Phys.* **18**, 840 (1950).

² Longworth, *Ann. N. Y. Acad. Sci.* **46**, 212 (1945).

³ Chandrasekhar, *Rev. Mod. Phys.* **15**, 2 (1943).

Reinvestigation of the Reaction Involving Nitrogen Pentoxide and Nitric Oxide

HAROLD S. JOHNSTON AND ROBERT L. MILLS

Department of Chemistry, Stanford University, Stanford, California

May 12, 1950

IT was suggested recently¹ that the reaction between NO and N₂O₅ be restudied² to elucidate the mechanism of the decomposition of nitrogen pentoxide. During the past two years we have completed this reinvestigation over a 100,000-fold range of total pressure at 27°C. Limited work has been done at 0° and 40°. Special techniques³ for the study of fast reactions were required at high total pressures. Foreign gases such as CO₂ and N₂ were almost as effective as the reactants themselves in maintaining the high first-order rates.

At total pressures of 7000 mm (mostly N₂) the observed first-order rate constant was 0.25 sec.⁻¹ and the extrapolated value at limiting high pressure was 0.29 sec.⁻¹. The energy of activation at 7000 mm was 21 ± 1 kcal./mole. At total pressures of 0.07 mm the first-order rate constant divided by the total concentration of gases was 1.93 × 10⁶ cc/mole-sec., and its value extrapolated to zero pressure is 2.34 × 10⁸ cc/mole-sec. The energy of activation at limiting low pressure is 14.5 ± 0.5 kcal./mole. This study is thus the first for which at one temperature both the high pressure limit and the low pressure limit of a unimolecular reaction have been essentially attained.

The mechanism proposed by Smith and Daniels² for the reaction of NO and N₂O₅ and the mechanism proposed by Ogg⁴ for the decomposition of N₂O₅ alone have been confirmed and extended. Analysis of the mechanism shows that the rate of the initial reaction of N₂O₅ and NO is that of the elementary unimolecular decomposition



The rate constants can be expressed in terms of reasonable values of "effective number of oscillators" and molecular cross sections. Some of the anomalies associated with the decomposition of N₂O₅ appear to be removed by these mechanisms and this experimental confirmation of them.

A complete summary of these data, a review of the decom-

position of N₂O₅, and an examination of theories of unimolecular reactions will be submitted to the appropriate journals in the near future.

¹ R. A. Ogg, Jr., *J. Chem. Phys.* **18**, 572 (1950); Ogg, Richardson, and Wilson, *J. Chem. Phys.* **18**, 573 (1950).

² J. H. Smith and F. Daniels, *J. Am. Chem. Soc.* **69**, 1735 (1947).

³ H. S. Johnston and D. M. Yost, *J. Chem. Phys.* **17**, 386 (1949).

⁴ R. A. Ogg, Jr., *J. Chem. Phys.* **15**, 613 (1947).

Theoretical Explanation of the Chemical Effects of Ultrasonics

VIRGINIA GRIFFING

Department of Chemistry, Catholic University of America, Washington, D. C.

May 19, 1950

RECENT investigations in this laboratory of chemical reactions induced by high intensity sound waves have led to the following qualitative explanation of these phenomena. In order to be specific, consider the experimental facts, already reported in the literature,¹ that under certain conditions water saturated with carbon tetrachloride will release free chlorine upon irradiation with high intensity ultrasonic waves. This reaction will not take place unless there is a gas dissolved in the solution. Furthermore, at a given intensity it will take place with certain gases in the solution such as He, N₂, and O₂ but will not occur when CO₂ is dissolved in the solution. These results have been verified for the experimental conditions in this laboratory and in addition it has been shown that Ne, Ar, and Xe also give the effect whereas no reaction occurs when the solution is saturated with N₂O, SF₆, or CCl₂F₂.

In order to explain these data, it is assumed that a gas dissolved in the solution forms also minute bubbles in the sound field. The liquid serves as an efficient transducer which carries the energy of the high intensity sound wave from the source to the interfaces between the small bubbles and the liquid. In the adiabatic compression of a sound wave, the production of a high temperature is dependent upon the existence of a large difference between the adiabatic and isothermal compressibility. As the sound wave travels through the liquid, the temperature difference due to the adiabatic compression is of the order of a degree centigrade while at these intensities a small bubble of gas may be compressed to half its volume producing a temperature variation of several hundred degrees. A temperature gradient in the gas bubble is then set up, which produces appreciable periodic temperature variation in the liquid adjoining the gas bubble.² If the intensity is sufficiently high, the temperature variation in the liquid adjoining the bubble is sufficiently great to cause the chemical reaction to take place. The same thermal processes are responsible for the loss of acoustic energy.

According to this idea, two thermal properties of the gas content of the bubbles are important. Firstly, $(\gamma - 1)$ will determine the temperature reached in the compressed bubble. As the γ of the gas approaches that of the liquid, the temperature reached becomes much lower. This explains why vapors such as ether inhibit these reactions even if the solution is saturated with air. Secondly, the thermal conductivity of the gas will determine how much the high gas temperature affects the liquid. In a case in which the reaction occurs in the gas phase, the thermal conductivity of the gas should be much less important or have the opposite effect.

Experimental and theoretical work is in progress in this laboratory to test the validity of this theory. About twenty gases are being tested having thermal properties which would place them either in a class with N₂ as gases which can bring about reactions or with N₂O which does not cause chemical reactions to take place. The rare gases make it possible to study the effect of thermal conductivity relatively independent of the specific heat. On the basis of this theory one would predict that Xe lies between N₂ and N₂O; one actually finds that less free chlorine is produced when the water is saturated with Xe than with N₂. Up to the present time all the known experimental facts fit these ideas

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).

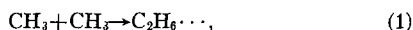
² These ideas were stimulated by a talk given in the Catholic University Physics Department by Richard R. Carhart, of the California Institute of Technology. His talk was taken from his Ph.D. thesis "Theory of viscous and thermal attenuation of sound by small spheres."

The Rate Constant of the Methyl Radical Recombination Reaction

ROBERT GOMER*

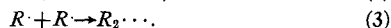
Gibbs Chemical Laboratory, Harvard University, Cambridge, Massachusetts
May 18, 1950

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

RICHARD M. BADGER AND M. KENT WILSON*

Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California
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.

* Present address: Mallinckrodt Chemical Laboratory, Harvard University.

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

Notice

THE *Journal of Chemical Physics* is a research journal intended to provide a medium for the publication of research results in the field of chemical physics. The Journal is published by the American Institute of Physics. The only income of the Journal is from subscriptions, from the page charge levied on institutions supporting the research which is published in the Journal, provided they wish to honor the charge, and minor income from the sale of back numbers, etc. The amount of material which can be accepted in the

Journal is, in the long run, limited by the subscription income.

Recent increases in the cost of printing and a very considerable increase in the number of manuscripts submitted to the editor's office have resulted in this limitation becoming very real. Individuals who are interested in the health and growth of the Journal will aid this by subscribing to the Journal or by bringing the opportunity to subscribe to the attention of others who may be interested in the Journal.