

## Comments on the Kinetics of Thermal Decomposition of Nitric Oxide

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## Comments on the Kinetics of Thermal Decomposition of Nitric Oxide

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 (Received January 6, 1953)

KAUFMAN and Kelso<sup>1</sup> describe some experimental measurements on the rate of thermal decomposition of nitric oxide in which they are unable to observe the pronounced catalytic influence of oxygen on the reaction kinetics of nitric oxide as previously reported by us.<sup>2</sup> Such a catalytic effect has been noted by Vetter;<sup>3</sup> it is also suggested by the results of Gilbert and Daniels.<sup>4,5</sup> In an attempt to resolve this discrepancy Kaufman and Kelso point to the possibility of an error in our analysis of the products of decomposition.

Since we are quite aware of such sources of error as encountered by them,<sup>6,7</sup> our experimental technique<sup>2,8</sup> is so designed to transfer all the reaction products from the reactor into a cold trap by means of a Toepler pump circuit. Subsequently, after the oxygen has been allowed to react with residual nitric oxide at room temperature, and the  $\text{NO}_2 = \text{N}_2\text{O}_4$  thus produced has been condensed out in a trap cooled by liquid nitrogen, the remaining noncondensable gas—i.e.,  $\text{N}_2$ —is pumped off quantitatively into a gas burette.\* Mass spectrometric analysis of this noncondensable gas indicated the absence of oxygen.

In contrast to this technique, the measurements of Kaufman and Kelso<sup>1</sup> differ not only in the experimental method of transfer of the reacted gas mixture, but also in the analysis of the noncondensable products. It is apparent that the pressure registered on their manometer<sup>1</sup> must be due to  $\text{N}_2$  and  $\text{O}_2$ . Such a determination, therefore, involves the measurement of a small pressure difference representing the amount of  $\text{N}_2$  and  $\text{O}_2$  produced from the decomposition of  $\text{NO}$ . An unknown quantity of the oxygen present in the mixture may react with residual  $\text{NO}$  during the transfer and cooling process, thereby decreasing the total amount of noncondensable gas. Also, the entrainment of noncondensable gas in the relatively large amounts of  $\text{CO}_2$  used by Kaufman and Kelso may further result in producing an apparently lower decomposition rate.

Although the decomposition of  $\text{NO}$  at  $1150^\circ\text{K}$  has been shown to be predominantly heterogeneous,<sup>8</sup> the authors neglect to consider the smaller surface-to-volume ratio ( $S/V$ ) of their reaction vessel, as compared to the one used by us.

For pure nitric oxide our measurements<sup>2</sup> of the decomposition rate exceed by 50 percent those reported by Kaufman and Kelso,<sup>1</sup> which is in line with the difference in  $S/V$  of the reaction vessels employed in these two investigations. It also appears from our results reported in Table II of reference 2 that the catalytic influence of oxygen on the rate of decomposition of nitric oxide is more pronounced at  $980^\circ\text{K}$ , than at  $1150^\circ\text{K}$  suggesting a heterogeneous catalysis in this temperature region. Thus the difference in  $S/V$  of the reaction vessels may be responsible for the apparent disagreement reported.<sup>1</sup>

It should be pointed out that the experimental measurements by Vetter<sup>3</sup> on the reaction rate of nitric oxide in the presence of oxygen at  $1179^\circ\text{K}$  definitely indicate the catalytic influence of oxygen contrary to the conclusions of Kaufman and Kelso.<sup>1</sup> Based on the rate constant as given by Fig. 2 of reference 2, the decomposition rate of  $\text{NO}$  in the absence of  $\text{O}_2$  amounts to  $1 \times 10^{-10}$  mole  $\text{cc}^{-1} \text{sec}^{-1}$  at  $1179^\circ\text{K}$ , whereas Vetter, in the presence of oxygen, measured a rate of  $3 \times 10^{-10}$  mole  $\text{cc}^{-1} \text{sec}^{-1}$ .

Concerning the questions raised on the proposed mechanism, it is well known that the observed specific reaction rates of many unimolecular reactions are several orders of magnitude larger than those calculated from the collision theory equation. Particularly in those reactions in which the reactant undergoing unimolecular decomposition may acquire its energy by transfer of kinetic energy from a foreign gas ( $M$ ) with subsequent conversion of this energy into vibrational energy, it is questionable whether simple collision theory offers an adequate quantitative picture of the process.

The relative efficiency of various gases in facilitating the recombination of halogen atoms<sup>9</sup> may be cited as an example.

One may conclude therefore that a more refined analysis is required to calculate the relative magnitudes of the terms appearing under the square-root sign of the final rate expression (4) of reference 2. Under these circumstances a comparison of rate constants based on collision theory is of little significance.

It also should be noted that the final form of the rate expression (4) may be obtained if one assumes the concentration of oxygen atoms to be given by the equilibrium between oxygen atoms and molecules. Such a condition would be favored by high concentrations of oxygen in agreement with the assumption made in deriving Eq. (4).

<sup>1</sup> F. Kaufman and G. R. Kelso, *J. Chem. Phys.* **21**, 751 (1953).

<sup>2</sup> H. Wise and M. F. Frech, *J. Chem. Phys.* **20**, 1724 (1952).

<sup>3</sup> K. Vetter, *Z. Elektrochem.* **53**, 269 (1949).

<sup>4</sup> Gilbert and Daniels, *Ind. Eng. Chem.* **40**, 1719 (1948).

<sup>5</sup> H. Wise and Baker, (to be published).

<sup>6</sup> Fenimore and G. R. Kelso, *J. Am. Chem. Soc.* **74**, 1593 (1952).

<sup>7</sup> F. Kaufman and G. R. Kelso, *J. Am. Chem. Soc.* **74**, 2694 (1952).

<sup>8</sup> H. Wise and M. F. Frech, *J. Chem. Phys.* **20**, 22 (1952).

\* A correction is applied for the vapor pressure of nitric oxide at the temperature of liquid nitrogen.

<sup>9</sup> E. Rabinowitch and W. C. Wood, *J. Chem. Phys.* **4**, 497 (1936).

## Microwave Spectrum and Structure of $\text{SiD}_3\text{F}$

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 (Received January 23, 1953)

THE problem of determining the structure of silyl fluoride has been attacked by Sharbaugh, Thomas, and Pritchard,<sup>1</sup> who observed microwave absorption frequencies for  $\text{Si}^{28}\text{H}_3\text{F}$ ,  $\text{Si}^{29}\text{H}_3\text{F}$ , and  $\text{Si}^{30}\text{H}_3\text{F}$ . The three structural parameters could, however, not be computed without taking the angle  $\text{HSiH} = 111^\circ \pm 1^\circ$  from other monohalogen silanes. We have prepared  $\text{SiD}_3\text{F}$  (by the action of  $\text{SbF}_3$  on  $\text{SiD}_3\text{Cl}$ ) and measured the absorption frequencies of the three isotopic species in order that the structure may be found exclusively by means of microwave measurements.

As pointed out by Miller, Aamodt, Dousmanis, and Townes<sup>2</sup> in the case of the methyl halides the effect of the zero-point vibrations cannot be neglected. The main effect is that the Si—H distance is larger than the Si—D distance and that the angle H—Si—H differs from the angle D—Si—D. If the large moment of inertia is denoted by  $I_B^D$ ,<sup>30</sup> for the molecule  $\text{Si}^{30}\text{D}_3\text{F}$ ,  $I_B^H$ ,<sup>28</sup> for  $\text{Si}^{28}\text{H}_3\text{F}$ , etc., and if the small moment of inertia is called  $I_A^H$  for the "light" compounds,  $I_A^D$  for the "heavy" compounds, we have

$$[I_B^{D,28} - \frac{1}{2}I_A^D]m_{\text{Si}^{28}\text{D}_2\text{F}} = a^2m_Fm_{\text{Si}^{28}} + 3(a+d_D \cos \varphi_D)^2m_Dm_F + 3d_D^2 \cos^2 \varphi_D m_{\text{Si}^{28}}m_D, \quad (1)$$

where  $m_{\text{Si}^{28}\text{D}_2\text{F}}$ , etc. means the mass of  $\text{Si}^{28}\text{D}_3\text{F}$ ,  $a$  is the Si—F distance (assumed to be independent of isotopic substitution),  $d_D$  is the distance Si—D, and  $\varphi_D$  is the supplementary angle of the F—Si—D angle.  $I_A^D = 3m_Dd_D^2 \sin^2 \varphi_D$ . Besides (1) there are 5 similar equations to be fulfilled by the experimental results given in Table I.

By suitable combination of four of the six equations mentioned above, one gets

$$a = \frac{m_H m_D}{m_F(m_D - m_H)} \left[ \frac{(I_B^{H,30} - I_B^{H,28})m_{\text{Si}^{30}\text{H}_2\text{F}}m_{\text{Si}^{28}\text{H}_2\text{F}}}{m_H^2(m_{\text{Si}^{30}} - m_{\text{Si}^{28}})} - \frac{(I_B^{D,30} - I_B^{D,28})m_{\text{Si}^{30}\text{D}_2\text{F}}m_{\text{Si}^{28}\text{D}_2\text{F}}}{m_D^2(m_{\text{Si}^{30}} - m_{\text{Si}^{28}})} + 3(d_H \cos \varphi_H - d_D \cos \varphi_D) \right] \quad (2)$$

together with two other analogous expressions for  $a$ , in which data for the  $\text{Si}^{29}$ -containing isotopes are used in connection with data for the  $\text{Si}^{28}$ - and  $\text{Si}^{30}$ -containing molecules. If the difference

TABLE I. Observed microwave absorption frequencies for isotopic silyl fluoride molecules (transition  $J=0 \rightarrow 1$ ).

Species	$\nu$ MHz	$I_B \times 10^{40}$ g cm <sup>2</sup>	$B$ MHz
Si <sup>29</sup> H <sub>3</sub> F	28655.8	0.1	58.555
Si <sup>29</sup> H <sub>2</sub> F	28393.4	0.2	59.096
Si <sup>29</sup> H <sub>3</sub> F	28145.2	0.2	59.617
Si <sup>29</sup> D <sub>3</sub> F	24507.0	0.1	68.467
Si <sup>29</sup> D <sub>2</sub> F	24352.2	0.1	68.902
Si <sup>29</sup> D <sub>3</sub> F	24204.5	0.2	69.323

$d_H \cos \varphi_H - d_D \cos \varphi_D$  is neglected, one calculates  $a = 1.5935A$  [using (2)],  $a = 1.5941A$  (using Si<sup>29</sup>, Si<sup>30</sup>), and  $a = 1.5932A$  (using Si<sup>28</sup>, Si<sup>29</sup>). If the experimental uncertainty is taken into account, we get  $a = 1.5935 \pm 0.0045A$ . Now, if it is assumed that 0.01A and 1° are upper limits to  $d_H - d_D$  and  $\varphi_H - \varphi_D$ , respectively, 0.0096A becomes an upper limit to the error in  $a$ . This serves as a reason for investigating the solutions of the six fundamental equations mentioned in the interval from  $a = 1.5890$  to  $a = 1.6076$ . Inserting values of  $a$  from this interval in the expression

$$\frac{m_F}{m_D} - 3d_D \cos \varphi_D = \left[ \frac{(I_B^{D,30} - I_B^{D,28}) m_{Si^{29}D_3F} m_{Si^{29}D_2F}}{m_D^2 (m_{Si^{30}} - m_{Si^{28}})} \right]^{\frac{1}{2}}, \quad (3)$$

a series of corresponding values of  $d_D \cos \varphi_D$  is calculated. If these are inserted in (1) a corresponding series of  $I_A^D$  values is obtained. From  $I_A^D$  and  $d_D \cos \varphi_D$ ,  $d_D$  and  $\varphi_D$  can be calculated separately. Curves representing  $d_D$  and  $\varphi_D$  as functions of  $a$  can thus be drawn. The same can be done for  $d_H$  and  $\varphi_H$ . Taking the uncertainty caused by errors in the frequency determinations fully into account, one obtains the results given in Table II.

TABLE II. Assumed and calculated values of structural parameters.

Assumed values of		Calculated values of		$a$
$d_H - d_D$	$\varphi_D - \varphi_H$	$d_H, d_D$	$\varphi_H, \varphi_D$	
0.005A	7.5'	1.475-1.444A	70°24'-70°03'	1.5951-1.5967A
0.005A	15'	1.470-1.444A	70°39'-70°03'	1.5954-1.5967A
0.010A	15'	1.470-1.452A	70°39'-70°03'	1.5954-1.5958A
0.010A	30'	1.461-1.452A	70°40'-70°00'	1.5946-1.5947A

It is highly satisfactory that the calculated  $d_H$  and  $d_D$  values are close to 1.456 as found by Tindal, Straley, and Nielsen<sup>3</sup> in the case of SiH<sub>4</sub>. Also, the F-Si-H angle is found to be 109°26'-110°, close to the angle of the regular tetrahedron. Of course, the calculations tell nothing of the exact values of  $d_H - d_D$  and  $\varphi_D - \varphi_H$ . They show definitely, however, that these two quantities cannot be as large as 0.02A and 1°, respectively. Solutions for which  $\varphi_H > \varphi_D$  do exist. They correspond, however, to values of  $d_H$  in the 1.47-1.50A region which is less consistent with the value 1.456A found in SiH<sub>4</sub>.

<sup>1</sup> Sharbaugh, Thomas, and Pritchard, Phys. Rev. **78**, 64 (1950).

<sup>2</sup> Miller, Aamodt, Dousmanis, and Townes, J. Chem. Phys. **20**, 1112 (1952).

<sup>3</sup> Tindal, Straley, and Nielsen, Phys. Rev. **62**, 151 (1942).

## Microwave Spectrum and Structure of SiD<sub>3</sub>Cl

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THE pioneer work for silyl chloride has been done by Sharbaugh<sup>1</sup> and by Dailey, Mays, and Townes.<sup>2</sup> Their experimental data together with data for SiD<sub>3</sub>Cl (prepared by the action of DCl on SiD<sub>4</sub>) are given in Table I. In a previous paper<sup>3</sup> the structure of silyl fluoride was discussed. The microwave absorption frequencies used in the calculations belong to a  $J=0 \rightarrow 1$  transition. Owing to zero-point vibrations, it was assumed that the distances Si-H ( $d_H$ ) and Si-D ( $d_D$ ) and the angles F-Si-H (180- $\varphi_H$ ) and F-Si-D (180- $\varphi_D$ ) deviated slightly ( $d_H > d_D$ ,  $\varphi_D > \varphi_H$ ). If a reasonable interpretation of the experimental

TABLE I. Observed microwave absorption frequencies for isotopic silyl chloride molecules (transition  $J=1 \rightarrow 2$ ).

Species	$\nu$ MHz*	$I_B \times 10^{40}$ g cm <sup>2</sup>	$B_0$ (MHz)
Si <sup>29</sup> H <sub>2</sub> Cl <sup>35</sup>	26695.2 ± 0.2	125.711	66673.8
Si <sup>29</sup> H <sub>3</sub> Cl <sup>35</sup>	25943.2	—	129.355
Si <sup>29</sup> H <sub>2</sub> Cl <sup>37</sup>	26049.6	—	128.826
Si <sup>29</sup> D <sub>2</sub> Cl <sup>35</sup>	23670.8	—	141.773
Si <sup>29</sup> D <sub>3</sub> Cl <sup>35</sup>	23402.6	—	143.397
Si <sup>29</sup> D <sub>2</sub> Cl <sup>37</sup>	23147.9 ± 0.3	144.975	5787.0
Si <sup>29</sup> D <sub>3</sub> Cl <sup>37</sup>	23091.4 ± 0.2	145.330	5772.8

\* Corrected for spin influence.

material of Table I is attempted, additional difficulties emerge. Probably this is due to the effect of centrifugal distortion. At a  $J=1 \rightarrow 2$  transition, the centrifugal distortion term in the expression for the rotational energy is 8 times greater than for a  $J=0 \rightarrow 1$  transition. The correct way out is, of course, to study the absorption of silyl chloride at 11 500-13 500 MHz and/or at 34 500-40 000 MHz, but as this is not possible with our present equipment we have had to proceed in the following manner:

We define

$$K^{30-28, H, 35} = \left[ \frac{(I_B^{30, H, 35} - I_B^{28, H, 35}) m_{Si^{30}H_2Cl^{35}} m_{Si^{28}H_2Cl^{35}}}{m_H^2 (m_{Si^{30}} - m_{Si^{28}})} \right]^{\frac{1}{2}},$$

where  $I_B^{30, H, 35}$  is the large moment of inertia of Si<sup>30</sup>H<sub>2</sub>Cl<sup>35</sup>. It follows for a rigid rotor that

$$a_H \frac{m_{Cl^{35}}}{m_H} - 3d_H \cos \varphi_H = K^{30-28, H, 35},$$

$$a_D \frac{m_{Cl^{35}}}{m_D} - 3d_D \cos \varphi_D = K^{30-28, D, 35},$$

$$a_H \frac{m_{Si^{29}H_2}}{m_H} + 3d_H \cos \varphi_H = K^{28, H, 37-35},$$

$$a_D \frac{m_{Si^{29}D_2}}{m_D} + 3d_D \cos \varphi_D = K^{28, D, 37-35},$$

where  $a_H$  and  $a_D$  are the Si-Cl distances in the "light" and "heavy" species. Addition of (1) and (3) now produces an equation giving  $a_H$  as a function of measured quantities. We find that  $2.0498A < a_H < 2.0507A$ . Similarly,  $a_D$  may be calculated. It is highly satisfactory that the result becomes  $2.0495A < a_D < 2.0507A$ .

Now,  $d_H \cos \varphi_H$  can be calculated from (1) for values of  $a$  in the interval indicated. Likewise, the small moment of inertia,  $I_A^H$ , can be found from, e.g.,

$$I_B^{28, H, 35} - \frac{1}{2} I_A^H = a_H^2 \frac{m_{Cl^{35}} m_{Si^{28}}}{m_{Si^{28}H_2Cl^{35}}} + 3(a_H + d_H \cos \varphi_H)^2 \frac{m_H m_{Cl^{35}}}{m_{Si^{28}H_2Cl^{35}}} + 3d_H^2 \cos^2 \varphi_H \frac{m_H m_{Si^{28}}}{m_{Si^{28}H_2Cl^{35}}}.$$

Since  $I_A^H = 3m_H d_H^2 \sin^2 \varphi_H$ , a corresponding series of  $d_H \sin \varphi_H$  values are obtained so that curves representing  $d_H$  and  $\varphi_H$  as functions of  $a$  in the interval 2.0497-2.0509A can be drawn. In an analogous manner curves for  $d_D$  and  $\varphi_D$  are constructed. We now look for the points of the curves, where  $|d_H - d_D|$  and  $|\varphi_H - \varphi_D|$  are small. The main features are given in Table II. If our assumed

TABLE II. Calculated values of molecular parameters for silyl chloride.

$aA$	$d_H A$	$d_D A$	$d_D - d_H A$	$\varphi_H$	$\varphi_D$	$\varphi_D - \varphi_H$
2.0497	1.444	1.449	0.005	70°23'	70°38'	15'
2.0503	1.422	1.439	0.017	69°40'	70°23'	43'
2.0509	1.400	1.428	0.028	68°57'	70°06'	69'

rigid rotor was only disturbed by zero-point vibrations, one would expect  $d_H > d_D$ . The curves must be extrapolated slightly towards smaller  $a$  values ( $a = 2.0490A$ ) in order to satisfy this condition.