

## Reaction Mechanism of Ammonia Oxidation in Shock Waves

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Using the values  $B_0(\text{C}_2\text{H}_6)=0.66310\pm0.00007\text{ cm}^{-1}$  (Lafferty and Plyler<sup>5</sup>),  $B_0(\text{C}_2\text{D}_6)=0.45973\pm0.00008\text{ cm}^{-1}$  (recalculated from the infrared data given by Allen and Plyler<sup>6</sup>),  $A_0(\text{C}_2\text{H}_6)=2.671\pm0.005\text{ cm}^{-1}$  (Lepard *et al.*<sup>4</sup>) and  $A_0(\text{C}_2\text{D}_6)=1.3416\pm0.0009\text{ cm}^{-1}$  (Lepard *et al.*<sup>1</sup>), the above four equations were solved to determine the four structural parameters:

$$\angle\text{HCH}\equiv\angle\text{DCD}=107.8^\circ\pm0.2^\circ,$$

$$r_0(\text{C}-\text{C})=1.534\pm0.002\text{ \AA},$$

$$r_0(\text{C}-\text{H})=1.095\pm0.002\text{ \AA},$$

$$r_0(\text{C}-\text{D})=1.093\pm0.001\text{ \AA}.$$

The values of  $r_0(\text{C}-\text{H})$  for  $\text{C}_2\text{H}_6$  and  $r_0(\text{C}-\text{D})$  for  $\text{C}_2\text{D}_6$  are thus very close to  $r_0(\text{C}-\text{H})=1.09397\pm0.00005\text{ \AA}$  for  $\text{CH}_4$  (Herranz and Stoicheff<sup>7</sup>) and  $r_0(\text{C}-\text{D})=1.0918\pm0.0003\text{ \AA}$  for  $\text{CD}_4$  (Olafson *et al.*<sup>8</sup>). The value of  $r_0(\text{C}-\text{C})$  is close to the value  $1.533\pm0.003\text{ \AA}$  suggested by Bartell<sup>9</sup> as a reference standard for saturated molecules.

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<sup>1</sup> D. W. Lepard, D. M. C. Sweeney, and H. L. Welsh, *Can. J. Phys.* **40**, 1567 (1962).

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## Reaction Mechanism of Ammonia Oxidation in Shock Waves

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ALTHOUGH catalytic oxidation of ammonia has been studied extensively, few works on non-catalytic high-temperature oxidation are reported. Therefore, we carried out experiments to clarify the mechanism of ammonia oxidation at high temperatures using a shock-tube technique combined with ultraviolet absorption measurements of OH and NH radicals.

Experimental arrangement was much the same as reported previously.<sup>1</sup> Reaction mixtures were prepared

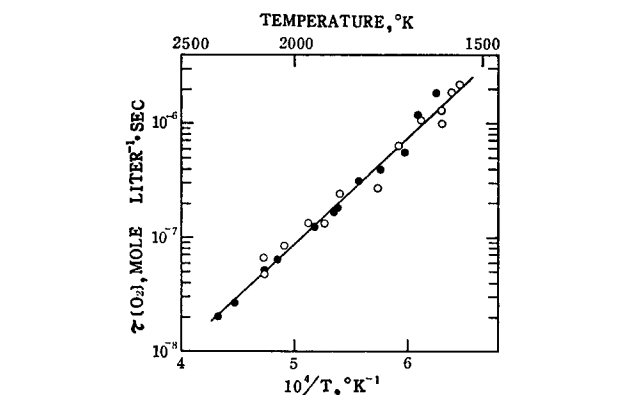


FIG. 1. Induction period vs reciprocal temperature. Open circles are obtained from mixture of 90% Ar, 4%  $\text{NH}_3$ , and 6%  $\text{O}_2$  and solid circles from 90% Ar, 6%  $\text{NH}_3$ , and 4%  $\text{O}_2$ . Solid line is least-squares line through the points.

in an all-glass apparatus and stirred magnetically for an hour before being used. Commercial ammonia (99.98%), oxygen (99.5%), and argon (99.99%) were used without further purification. Experiments were done with two mixtures in the range of conditions  $1550^\circ\leq T\leq 2300^\circ\text{K}$ ,  $3.5\leq P\leq 5.5\text{ atm}$  and  $7.41\times 10^{-4}\leq [\text{O}_2]\leq 2.47\times 10^{-3}\text{ mole/liter}$ .

Induction period for appearance of OH was found to be dependent upon oxygen concentration as shown in Fig. 1. The least-squares line in the figure is expressed by

$$\log\tau[\text{O}_2](\text{mole liter}^{-1}\cdot\text{sec}) = -11.71 + (9300\pm 270)/T,$$

the temperature dependence being  $42.5\pm 1.2\text{ kcal/mole}$ .

The ultraviolet absorption of NH at  $3360\text{ \AA}$  ( $^3\Pi-^3\Sigma$  band) was measured for several runs by using the same optical arrangement as that for OH absorption measurement. As shown in Fig. 2, the general behaviors of both absorptions are: (a) both absorptions appear almost at the same time, (b) NH absorption becomes maximum earlier than OH absorption does, and (c) NH

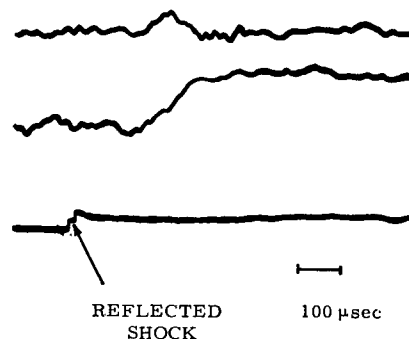
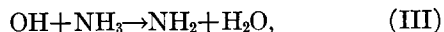


FIG. 2. Change of OH and NH absorption with time. Uppermost trace represents NH absorption, middle trace OH, and bottom trace pressure.  $T: 1840^\circ\text{K}$ ;  $P_1: 65.0\text{ mm Hg}$ ; composition of mixture: 90% Ar, 6%  $\text{NH}_3$ , and 4%  $\text{O}_2$ ; sweep rate:  $100\text{ }\mu\text{sec/division}$ .

disappears within a few tens of microseconds, while OH remains at its maximum for a few milliseconds.

From these experimental results, we propose the following reaction scheme as operating mainly during the induction period of high-temperature oxidation of ammonia:



where Reaction (I) is the most endothermic; if the bond energies of NH-H and H-O<sub>2</sub> are taken to be, respectively, 88<sup>2-5</sup> and 47<sup>6</sup> kcal/mole, its endothermicity should be 41 kcal/mole. The activation energy of 42.5 kcal/mole obtained in the present experiment suggests that this step is rate controlling. Also, findings (a)-(c) support the existence of Reactions (I) and (II) which are followed by Reaction (III) to regenerate NH<sub>2</sub>.

The present scheme is quite different from that proposed by Husain and Norrish<sup>7</sup> to be responsible for the photolytic oxidation, in which HNO is supposed to be a degenerate branching reagent. However, our scheme seems more reasonable to explain the present results in shock waves.

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<sup>2</sup> This value is calculated from the values of the bond energies of NH<sub>2</sub>-H and N-H and of the average N-H bond energy in ammonia; they are taken to be 106,<sup>3</sup> 85<sup>4</sup>, and 93<sup>5</sup> kcal/mole, respectively.

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## Molecular Quadrupole Moment of BrCN from Microwave Spectral Linewidth

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THE self-broadened widths of the pure rotational line  $J_2 \rightarrow 3$  in the ground vibrational state of the BrCN molecule have been theoretically calculated using Anderson's theory<sup>1</sup> as amplified by Tsao and Curnutte.<sup>2</sup>

The method of calculation is the same as followed for the self-broadening case of OCS.<sup>3</sup> The molecular interactions responsible for the linewidth in this case should be of the following types: dipole-dipole, dipole-quadrupole, quadrupole-dipole, quadrupole-quadrupole, dipole-induced dipole, quadrupole-induced dipole, dipole-induced quadrupole, and the first-order London dispersion forces. The exchange interaction will not be important in broadening the line because the presence of large electrostatic interactions ( $\mu_{\text{BrCN}} = 2.94 \times 10^{-18}$  esu) limits the intermolecular separations to larger values than the separation corresponding to the minimum potential energy where the exchange forces dominate. Smith *et al.*<sup>4</sup> tried to explain the width and its temperature dependence<sup>5</sup> by considering the dipole-dipole interaction as responsible for the broadening due to the lower  $J_2$  ( $J_2 < 20$ ) transitions of the perturbing molecules and considering only approximately the dipole-quadrupole interaction for broadening due to the higher  $J_2$  ( $J_2 > 20$ ) transitions of the perturbing molecules. They gave a value  $20.2 \times 10^{-26}$  esu for the molecular quadrupole moment of BrCN. Their calculated linewidth at 228°K is 22M lower than the experimental value.

In the present note the quadrupole moment of the BrCN molecule has been re-evaluated by considering all the possible molecular interactions responsible for the linewidth. The expressions for the collision interruption function  $S_2(b)$  and the collision cross section  $\sigma$  due to the different interactions are now available in the literature.<sup>2,6-8</sup>

The relative contributions of the different interactions in  $S_2(b)$  for  $b=b_0$ , where  $S_2(b)=1$ , are given in Table I for  $q_{\text{BrCN}} = 20.0 \times 10^{-26}$  esu. It is apparent that  $\mu_1-\mu_2$  interaction is mostly responsible for the broadening for low  $J_2$  values. But for higher  $J_2$  values, the  $\mu_1-q_2$  and  $q_1-\mu_2$  interactions can never be neglected. However, the  $q_1-q_2$  interaction contributes only 5% to 6% at the most, which will not interrupt the radiation materially. The interactions due to the induction and dispersion forces can, of course, be neglected completely.

The variation of the calculated linewidth with the quadrupole moment at the two temperatures is shown in Fig. 1. It is observed that while at 228°K the quadrupole moment of the molecule giving exact fit with the data is  $21.5 \times 10^{-26}$  esu, at 373°K this is only  $5.5 \times 10^{-26}$  esu. Thus, no single value of the quadrupole moment could explain the temperature dependence of

TABLE I. The relative contributions of the different interactions in  $S_2(b)$  for  $b=b_0$  where  $S_2(b)=1$  for  $q_{\text{BrCN}} = 20.0 \times 10^{-26}$  esu.

$J_2$	$b_0$ (in Å)	$S_2(b)_{\mu_1-\mu_2}$	$S_2(b)_{\mu_1-q_2}$	$S_2(b)_{q_1-\mu_2}$	$S_2(b)_{q_1-q_2}$	$S_2(b)_{\mu_1-\alpha_2\mu_1}$	$S_2(b)_{\mu_1q_1\alpha_2}$	$S_2(b)_{diss}$
0	43.8	0.9974	0.0040	0.0026	0.0000	0.0000	0.0000	0.0000
10	28.1	0.9018	0.0381	0.0446	0.0009	0.0000	0.0000	0.0000
20	18.5	0.3469	0.4363	0.1988	0.0220	0.0000	0.0000	0.0000
30	16.3	0.0186	0.8995	0.0356	0.0598	0.0001	0.0001	0.0002
40	16.2	0.0000	0.9330	0.0000	0.0625	0.0001	0.0001	0.0002