

In the limit of zero applied voltage one can substitute the empirical expression for  $F$  into Eq. (3) and deduce that a Schulz mass spectrum yields  $\Phi - F = 0.155[\psi(b+3) - \ln(b+2)]$  where  $\psi$  is the logarithmic derivative of the gamma function. In principle this allows measurement of sample polydispersity without going to large  $|\eta|$  as required by the "method of moments,"<sup>2</sup> but this more difficult method will probably be seldom required. For large positive  $\eta$  the difference  $\Phi - F$  becomes large, but the moments method is more sensitive. For negative  $\eta$  the moments method is rather insensitive and this method might be useful, but  $\Phi - F$  is difficult to express except numerically.

<sup>1</sup> A. Peterlin and M. Ribarič, *J. Chem. Phys.* **31**, 759 (1959).

<sup>2</sup> A. Prock and G. McConkey, *J. Chem. Phys.* **32**, 224 (1960).

<sup>3</sup> H. Carslaw and J. Jaeger, *Proc. London Math. Soc.* **46**, 383 (1939).

<sup>4</sup> G. Watson, *Theory of Bessel Functions* (Macmillan Company, New York, 1944), p. 345.

### Nonmolecular Nature of Nitric-Oxide-Inhibited Thermal Decomposition of *n*-Butane

ARON KUPPERMANN AND JOHN G. LARSON

*Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois*

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THE thermal decomposition of most organic molecules is generally accepted to occur at least in part via a free radical chain process. Since Hinshelwood and Staveley<sup>1</sup> discovered that small additions of nitric oxide reduced the rate of thermal decomposition, there has been much controversy<sup>2</sup> concerning the nature of the "residual" reaction remaining after further additions of inhibitor produce no further decrease in rate. Jach, Stubbs, and Hinshelwood<sup>3</sup> have shown this limiting rate to be independent of the inhibitor used and attribute this residual reaction to a nonchain molecular process in which the parent molecule breaks up, in a single step, into stable products.

Wall and Moore<sup>4</sup> and later Rice and Varnerin<sup>5</sup> studied isotopic exchange in the thermal decomposition of ethane and ethane-*d*<sub>6</sub> and found extensive mixing in both the inhibited and normal decompositions. In building a case for concluding that the limiting rate corresponds to the complete suppression of chains and hence to a unimolecular split into stable molecules, Hinshelwood<sup>6</sup> discounts the results of Wall and Moore for not using sufficient inhibitor to produce complete inhibition, and the results of Rice and Varnerin on the grounds that the mixing they observe may result from a secondary process involving the methylene radical formed in the split-off of methane from ethane. He suggests that methylene may not be easily scavenged by NO and thus that the isotopic mixing may be due to this atypical decomposition in which one product is a stable molecule and the other a diradical.

Semenov,<sup>7</sup> in quoting work by Voedvodsky, explains complete inhibition as the using up of free valencies on the surface of the reaction vessel which would normally produce a higher gas-phase-radical concentration. Voedvodsky<sup>8</sup> has suggested that two heterogeneous initiation processes, a reversible and an irreversible one, satisfactorily explain experimental observations.

If this limiting rate corresponds to a unimolecular process, then there exists a good set of unimolecular reactions for study. If the residual reaction is of the chain variety, then inhibition may shed some light on the mechanism of chain initiation. In either case, it is important to clearly establish the nature of this residual reaction.

In order to obtain unequivocal information about this residual reaction, we have investigated the thermal decomposition of a mixture of *n*-butane and *n*-butane-*d*<sub>10</sub> in the absence and presence of NO. About 10 cm Hg pressure of an equimolar mixture of these butanes was decomposed in a 100-ml pyrex reaction vessel to extents varying from about 1% to 5%. A temperature of about 430°C was selected so that the reaction could be stopped at small percentages of decomposition. The product-reactant mixture was analyzed with the help of a mass spectrometer. The ratio of ion currents at *m/e* values 20 and 68 (after a small contribution from the unreacted mixture to the current at *m/e* 20 was subtracted) was taken as a measure of the extent of decomposition. The latter was also determined by the pressure change in the reaction vessel. The CD<sub>3</sub>H/CD<sub>4</sub> ratio was determined from a liquid nitrogen non-condensable fraction of the reacted mixture. This ratio was found not to change as the fractional decomposition varied from 5% down to 1%, which was the lowest value for which reliable measurements could be made. It was further found that this ratio did not change if the reaction was inhibited by initially adding NO to the reaction mixture in amounts variable between 13.4 and 27.6 mole-percent, although this added NO decreased the decomposition-rate-constant by a factor of 3.4. The average CD<sub>3</sub>H/CD<sub>4</sub> ratio was 2.38±0.04 for fifteen uninhibited runs and 2.36±0.04 for fifteen inhibited runs. Conditioning of the vessel by twelve successive runs with pure *n*-butane did not, within the accuracy of the experiments, change the rate constants or the CD<sub>3</sub>H/CD<sub>4</sub> ratios. A sixty fold increase in the surface to volume ratio, obtained by packing the vessel with pyrex wool, had no detectable effect on the rate-constant or the CD<sub>3</sub>H/CD<sub>4</sub> ratio of the uninhibited runs.

In order to eliminate the possibility that the formation of isotopically mixed methanes in the inhibited reaction might be due to secondary processes, mixtures of 5.15% CD<sub>4</sub> and 94.85% C<sub>4</sub>H<sub>10</sub> were reacted in the absence of NO and in the presence of 15.4% of NO, under the same experimental conditions described above, until about 5% of the C<sub>4</sub>H<sub>10</sub> decomposed. No formation of CD<sub>3</sub>H whatsoever was detected. This

entirely excludes the possibility of mixing of molecularly formed  $CD_4$  by any subsequent secondary processes, whether heterogeneous or gas phase, under these experimental conditions.

If the inhibited reaction were entirely molecular, the corresponding  $CD_3H/CD_4$  ratio should be zero. Since, within experimental error, it was actually the same as in the uninhibited one, it may be clearly concluded that practically no (i.e., less than 2%) methane is formed by a direct split mechanism in the NO-inhibited thermal decomposition of *n*-butane. This casts very serious doubts on the validity and consequences of the conclusions previously reached<sup>8,9</sup> that inhibited reactions of this type were entirely molecular. The results of the present experiments are, furthermore, not inconsistent with a heterogeneous initiation mechanism.<sup>7,8</sup>

<sup>1</sup> L. A. K. Staveley and C. N. Hinshelwood, Proc. Roy. Soc. (London) **A154**, 335 (1936).

<sup>2</sup> E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1954), p. 99.

<sup>3</sup> J. Jach, F. J. Stubbs, and C. Hinshelwood, Proc. Roy. Soc. (London) **A224**, 283 (1954).

<sup>4</sup> L. A. Wall and W. J. Moore, J. Am. Chem. Soc. **73**, 2840 (1951).

<sup>5</sup> F. O. Rice and R. E. Varnerin, J. Am. Chem. Soc. **76**, 324 (1954).

<sup>6</sup> C. Hinshelwood, Chem. Soc. (London), Spec. Publ. No. 9, (1957), 49.

<sup>7</sup> N. N. Semenov, *Some Problems of Chemical Kinetics and Reactivity* (Pergamon Press, New York, 1958), p. 248.

<sup>8</sup> V. V. Voedvodsky, Trans. Faraday Soc. **55**, 65 (1959).

<sup>9</sup> J. Jach and C. Hinshelwood, Proc. Roy. Soc. (London) **A229**, 143 (1955); *ibid.* **A231**, 145 (1955).

## Estimation of the Ionization Potential and Dissociation Energy of Molecular Astatine

ROBERT W. KISER

Department of Chemistry, Kansas State University,  
Manhattan, Kansas

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**T**HERE does not exist in the literature any directly measured value for the ionization potential or the dissociation energy of astatine. The ionization potential of At has been found to be 9.5 ev.<sup>1</sup> By using empirical correlations one may arrive at estimations of these values.

The values of  $\omega_e$  of 892, 565, 323, and 215  $cm^{-1}$  for  $F_2$ ,  $Cl_2$ ,  $Br_2$ , and  $I_2$ <sup>2</sup> allow the estimation of  $\omega_e \cong 160$   $cm^{-1}$  for  $At_2$ . By using the relation

$$\log \omega_e = a - b \log n^2 I \quad (1)$$

given by Varshni<sup>3</sup> for  $XX$  molecules, one estimates  $I(At_2) = 8.3$  ev, as shown in Fig. 1.  $n$  = principal quantum number and  $a$  and  $b$  are constants (or nearly so). Values of  $I(X_2)$  are 15.83, 11.48, 10.55, and 9.28, for  $F_2$ ,  $Cl_2$ ,  $Br_2$ , and  $I_2$ , respectively.<sup>4,5</sup>

The relation given by Mitra for  $XX$  molecules,

$$\log D = c + d \log I, \quad (2)$$

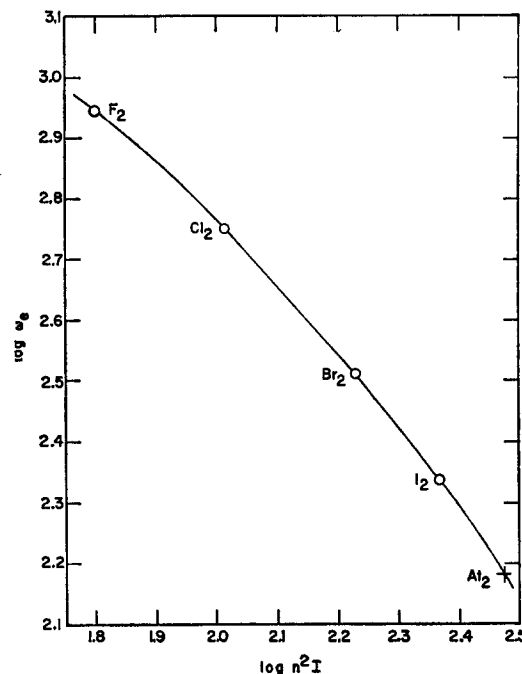


FIG. 1. Plot of the Varshni relation for the halogen molecules.

may be used to estimate the dissociation energy,  $D$ , of  $At_2$ . The curve of Eq. (2) is shown in Fig. 2, and is found to be remarkably linear, except for the data for  $F_2$  which have been omitted. Values of  $D(X_2)$  are 1.59, 2.47, 1.97, and 1.54 ev for  $F_2$ ,  $Cl_2$ ,  $Br_2$ , and  $I_2$ , respectively.<sup>6,7</sup> From Fig. 2,  $D(At_2) = 1.2$  ev.

The thermochemical cycle

$$D(X_2^+) = D(X_2) + I(X) - I(X_2) \quad (3)$$

may be used to calculate values of  $D(X_2^+)$ . Taking  $I(X)$  equal to 17.42, 13.01, 11.84, and 10.45 ev for  $X = F, Cl, Br,$  and  $I$ , respectively,<sup>8</sup> we find that  $D(X_2^+)$  is 3.18, 4.00, 3.26, 2.71, and 2.4 ev for  $X_2 = F_2, Cl_2,$

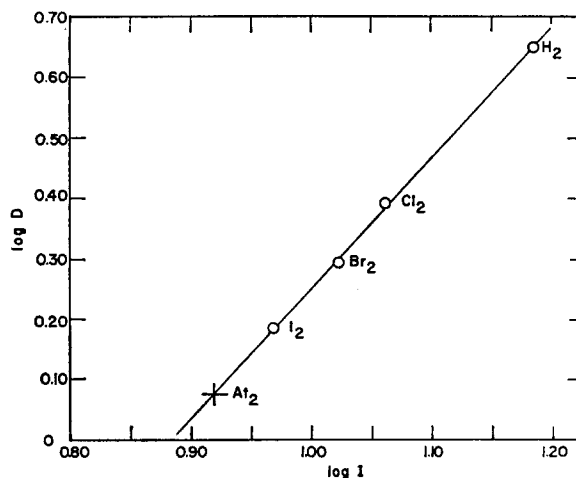


FIG. 2. Plot of the Mitra relation for the halogen molecules.