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THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few half-tone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the first of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$4.00 per page) will not be made and no reprints will be furnished free.

A Study of Metallic Electrodes Prepared by Sublimation

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January 20, 1949

A NUMBER of attempts have been made to prepare solid metals in a strain-free condition and to use them as reversible electrodes. A few authors have succeeded in preparing pure strain-free single crystals of zinc.¹ At least one paper by Clayton and Vosburgh² records the preparation of reversible zinc electrodes by careful annealing of a large piece of zinc. The latter authors compared their annealed electrodes to both surface amalgamated zinc and to saturated zinc amalgam. Silver chloride electrodes which are reversible have been prepared by reducing silver oxide thermally.³ The silver thus formed is in the form of a very finely divided spongy crystalline mass.

The following is an account of a study of electrodes prepared by evaporating zinc in vacuum. Pure zinc metal was vacuum sublimed on platinum wire set in the end of glass tubes. The zinc was deposited on the electrodes in the form of very finely divided loosely adhering crystals.

The electrodes, thus prepared, were placed in a dilute solution of pure zinc chloride saturated with basic zinc carbonate; air being rigidly excluded. Several sets of these cells were made at different times and the electromotive force measured. They usually agreed among themselves to within 25 to 30 microvolts. Very seldom did the difference exceed 70 microvolts. These cells were found to be stable for longer than eight weeks. The electrodes were not injured by storing in distilled water after they had been removed from a zinc chloride solution. However, when the same electrodes were reused return to equilibrium was slow—probably due to zinc chloride which was not washed out of the crystal aggregates. Cells using freshly prepared electrodes came to equilibrium almost at once.

The results so far obtained strongly indicate that zinc electrodes prepared in this way are free from strain and are reversible. It is hoped that this may be a general property of crystals formed in this way.

¹ F. H. Getman, J. Phys. Chem. **35**, 2749 (1931).² Clayton and Vosburgh, J. Am. Chem. Soc. **58**, 2013 (1936).³ Jones and Baecström, J. Am. Chem. Soc. **56**, 1524 (1934).

Isotope Effect in the Rupture of Carbon-Carbon Bonds in Propane-1-C¹³

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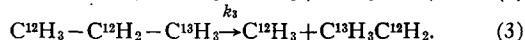
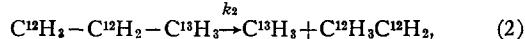
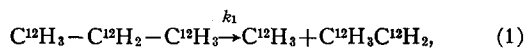
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January 7, 1949

R ECENT experiments have shown a significant isotope effect in the rupture of carbon-carbon bonds in propane-1-C¹³ by electron impact¹ as well as in thermal cracking.² It is difficult to understand the isotope effects in the thermal

cracking experiments in terms of some of the proposed mechanisms for the reaction. Thus such experiments may lead to a better understanding of the detailed mechanism. The isotope effect, 8 percent greater frequency of rupture of C¹²-C¹² than C¹²-C¹³ at ten percent cracking (14 percent for infinitesimal cracking³), is sufficiently large to permit a detailed investigation of the isotope effects.

The pyrolysis of propane is probably a chain reaction, and the over-all isotope effect in the depletion of propane as well as in the formation of individual products is the result of several consecutive and competing reactions. For a detailed interpretation of the mechanism, it is necessary to know the isotope effects in the various elementary reactions. To this end I have calculated an upper limit for the ratios of the rate constants in the rupture of the C-C bonds in propane according to the following reactions



The ratios of the rate constants $k_1/2k_2$ and $k_1/2k_3$ have been calculated by using an approximate equation derived⁴ by the application of the statistical mechanical treatment of isotopic molecules⁵ to the statistical treatment of absolute rates.⁶ The approximate equations for the ratios of the rate constants are

$$\frac{k_1}{2k_2} = \left\{ \frac{m_2^*}{m_1^*} \right\}^{\frac{1}{2}} \{ 1 + \sum_i 3^{n-6} G(u_i) \Delta u_i - \sum_i 3^{n-6} G(u_i \ddagger) \Delta u_i \ddagger \}, \quad (4)$$

$$\frac{k_1}{2k_3} = \left\{ \frac{m_3^*}{m_1^*} \right\}^{\frac{1}{2}} \{ 1 + \sum_i 3^{n-6} G(u_i) \Delta u_i - \sum_i 3^{n-6} G(u_i \ddagger) \Delta u_i \ddagger \}. \quad (5)$$

The function $G(u)$ has been previously defined;⁶ m^* is the effective mass of the activated complex along the reaction coordinate; $\Delta u_i = (hc/kT)(\omega_{1i} - \omega_{2i})$; and \ddagger is a property of the activated complex.

For the calculation of an upper limit to the isotope effect in the C-C bond rupture we assume that the skeletal vibrations are reduced to zero in the activated complex, and the remaining vibrations of the molecule are unaffected. That is, we assume that the activated complex consists of two essentially free methyl groups and one free methylene group. In such a model we should take into account that the C-H bonds will be stronger in the free methyl and methylene groups than in propane. Since this reduces the isotope effect, and the model of the activated complex is artificially chosen to give an upper limit, we shall neglect this effect.

The normal vibrations of propane have not yet been completely analyzed,⁷ and it is not possible to treat the skeletal vibrations independently of the rocking vibrations.^{8,9} Therefore the skeletal vibrations have been approximated using the force constants $k_{\text{C-C}} = 4.03 \times 10^5$ dynes/cm and $k_2 = 0.36 \times 10^5$ dynes/cm. This set of force constants gives a slightly better fit to the experimental data than those used by Abonen.¹⁰ For convenience in calculation, the isotope effect in the skeletal vibrations is calculated for the molecule C¹³H-C¹²H-C¹²H, and the vibrational isotope effect divided by 2. Thus the right-hand brackets in Eqs. (4) and (5) become $(1 + 1/2(G(u_1)\Delta u_1 + G(u_2)\Delta u_2 + G(u_3)\Delta u_3))$. The values of ω and $\Delta\omega$ calculated with the above force constants are

	ω	$\Delta\omega$
ω_1	918	14.6
ω_2	375	9.8
ω_3	1053	13.6

The ratios of the effective masses are calculated according to a recent treatment given by Slater.¹¹ In a unimolecular decomposition of a polyatomic molecule, the effective mass is the reduced mass of the two atoms connected in the bond being broken. The results of the calculation of an upper limit

of the isotope effect in the rupture of C—C bonds in propane are given in Table I.

TABLE I.

T°K	$k_1/2k_2$	$k_1/2k_3$
300	1.043	1.023
400	1.034	1.014
500	1.030	1.010
800	1.024	1.004

If one assumes that the various ion fragments smaller than $C_3H_3^+$ formed in the electron bombardment experiments arise from the decomposition of the latter, and that the skeletal vibrations of the ion are the same as those in the molecule (actually they should be smaller and thus the isotope effects somewhat reduced), then the isotope effects in the electron bombardment should be the same as those given in Table I. The significant discrepancy is that the ratio $k_1/2k_3$ found experimentally¹ is less than unity. A similar discrepancy exists in the ions formed from deuterio-methane. It is difficult to see how any mechanism which treats the production of ions as a rate process will remove this discrepancy. If one postulates that the C—H force constants are sufficiently greater in the above model of the activated complex than in the parent ion to reduce $k_1/2k_3$ below unity, then $k_1/2k_2$ will be sufficiently lower than the experimental value to give this procedure much weight.

¹ Beeck, Otvos, Stevenson, and Wagner, J. Chem. Phys. **16**, 255 (1948).
² See reference 1, p. 993.

³ J. Bigeleisen, unpublished calculations.

⁴ J. Bigeleisen, presented at the Brookhaven conference on kinetics, December 1, 1948.

⁵ J. Bigeleisen and M. G. Mayer, J. Chem. Phys. **15**, 261 (1947).

⁶ For a discussion of the statistical treatment of absolute rates see S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

⁷ See Gerhard Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), pp. 359 ff.

⁸ J. Bigeleisen, unpublished calculations.

⁹ L. Friedman and J. Turkevich, unpublished infra-red spectra of the deuterio-propanes.

¹⁰ C. A. Ahonen, J. Chem. Phys. **14**, 625 (1946).

¹¹ N. B. Slater, Proc. Roy. Soc. **194**, 112 (1948).

Dissociation Schemes of N_2 , P_2 , As_2 , Sb_2 , and Bi_2 *

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THE results in the NO spectrum which lead to a new dissociation scheme of NO^{1-3} make the revision of the N_2 dissociation energy also necessary. The re-examination of the observed dissociation phenomena in N_2 and N_2^+ yields, according to Schmid and Gerö,^{1,2} a dissociation scheme for N_2 in which the $N_2(^1\Sigma_g^+)$ ground state dissociates into $2D+2D$ atoms. The bond energy of the molecular ground state and the dissociation energy counted from the $4S+4S$ atomic term combination are given in the first line of Table I.

TABLE I.

	Bond energy, cm ⁻¹ energy height of $2D_{3/2}+2D_{3/2}$	Dissociation energy, cm ⁻¹ energy height of $4S+4S$
$N_2(^1\Sigma_g^+)$	78,750	40,350
$P_2(^1\Sigma_g^+)$	44,600	21,870
$As_2(^1\Sigma_g^+)$	34,540	13,360
$Sb_2(^1\Sigma_g^+)$	25,220	8,200
$Bi_2(^1\Sigma_g^+)$	15,860	-6,980

A review of the available experimental material for P_2 , As_2 , Sb_2 , and Bi_2 , in the light of this dissociation scheme of N_2 , results in new dissociation schemes for these molecules, according to which the molecular ground states are also

formed from $2D+2D$ atoms. The corresponding values of bond energies and dissociation energies are included in Table I.

In the P_2 spectrum the observed predissociation effects,⁴ at the $v'=10$, $J'=58$ and $v'=11$, $J'=34$ levels of the $1^1\Sigma_u^+$ state give, with the limiting-curve method, $51,965 \pm 25$ cm⁻¹ for the energy height of the predissociation limit. The dissociation scheme is obtained by identifying this limit with the energy height of the $2D+2P$ atomic term combination. The $4S+4S$ atomic term combination is slightly above the energy height of the last observed vibrational level of the $P_2(^1\Sigma_g^+)$ ground state at 21,830 cm⁻¹ with $v''=32$, explaining in this way the interruption of the observed bands at this vibrational quantum number.

In As_2 the given dissociation scheme can be obtained by ascribing the observed predissociation effects⁵ in the neighborhood of 42,700 cm⁻¹ to the effect of the $2D+2P$ term combinations. The splitting of these atomic term combinations makes it possible to explain the interruption of the bands from the B level with $v=8$ at 42,824 cm⁻¹ by the effect of the $2D_{5/2}+2P_{3/2}$ term combination, the interruption of the bands from the A level with $v=9$ at 42,578.7 cm⁻¹ by the effect of $2D_{3/2}+2P_{3/2}$, the predissociation effects of the A , $v=8$ and B , $v=6$ levels by the effect of $2D_{5/2}+2P_{1/2}$, and the interruption of the bands from the C level with $v=0$ at 42,006 cm⁻¹ by the effect of the $2D_{3/2}+2P_{1/2}$ atomic term combination. The energy height of the $2D_{3/2}+2D_{3/2}$ term combination is in good agreement with the extrapolated 31,726 cm⁻¹ bond energy value of the ground state. The interruption of the observed bands with the $v=70$ level of the $X(^1\Sigma_g^+)$ ground state at 24,085 cm⁻¹ can be explained by the presence of the $4S+2D_{3/2}$ atomic term combination at this energy height, whereas the energy height of the $4S+4S$ atomic term combination is between the $v=34$ and $v=35$ vibrational levels of the ground state, and in Fig. 1 of Almy and Kinzer's first paper, one can observe a sudden weakening of the intensity in this region.

The values given for Sb_2 result from attributing the predissociation effect observed by Naudé⁶ at $2842A = 35,200$ cm⁻¹ to the $2D_{3/2}+2P_{3/2}$ atomic term combination.

In Bi_2 , in identifying the predissociation effect³ of the C level at 37,026 cm⁻¹ with the energy height of the $2D_{3/2}+1P_{1/2}$ atomic term combination, the $4S+5P_{1/2}$ term combination yields as convergence limit for the bond energy of the C level 2490 cm⁻¹, whereas the value calculated by Almy and Sparks is 2500 cm⁻¹. In the neighborhood of the predissociation effect at the D level at 42,485 cm⁻¹ and of the slightly higher convergence limit of this level, the atomic term combinations are so numerous as a result of this coordination that one cannot decide which of them is responsible for the effects. The bond energy of the ground state counted from the $2D_{3/2}+2D_{3/2}$ term combination is 15,860 cm⁻¹, the bond energy of the B state counted from the $2D_{5/2}+2P_{1/2}$ term combination is 12,375 cm⁻¹. Almy and Sparks calculate by extrapolation for the bond energy of the ground state 14,900 cm⁻¹, while linear extrapolation would give 23,100 cm⁻¹; for the bond energy of the B state they calculate 11,516 cm⁻¹, the linear extrapolated value being 14,600 cm⁻¹.

The dissociation schemes of PO , AsO , SbO , and BiO should also show a corresponding analogy with that of NO , though there are much less available data for these molecules. According to the NO dissociation scheme of Schmid and Gerö,¹⁻³ the $NO(X^2\Pi)$ ground state dissociates into $N(^2D)+O(^3P)$ atoms with a bond energy of 53,800 cm⁻¹. The analogous term combination should also correspond to the convergence limit of the ground states of PO , AsO , SbO , and BiO . This view is fairly well supported by the increasing spin splitting of the $X^2\Pi$ -ground states of these molecules which is 120.9 cm⁻¹ for NO , 224 cm⁻¹ for PO , 1024 cm⁻¹ for AsO , 2272 cm⁻¹ for SbO . These are comparable with the spin splitting of the corresponding $2D$ terms which are 7 cm⁻¹ for N , 14.6 cm⁻¹ for P , 322.2 cm⁻¹ for As , 1341.6 cm⁻¹ for Sb , 4019 cm⁻¹ for Bi ,