

## The Sodium (2 P) PhotoSensitized Decomposition of Ethane

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out from  $q = -\infty$  to  $+\infty$ , the pressure can still remain low, fulfilling the condition under which the Freundlich isotherm is valid; and  $\int_{-\infty}^{+\infty} N(q) dq$  would therefore remain finite if Sips' reasoning were sound. The non-convergence character of  $\int_{-\infty}^{+\infty} N(q) dq$  is actually a consequence of Sips' use of Eq. (1) in which he contends that those sites where  $q = -\infty$  are not counted. Therefore the lower integration limit of  $\int N(q) dq$  should be some finite value instead of being  $-\infty$  in order to make the operation consistent. Such a change in limit makes the integral convergent at all pressures where the isotherm equation holds.

In conclusion, Sips' treatment can only be useful if (a) the Langmuir isotherm is valid and (b) the isotherm equation representing the true adsorption mechanism (and not merely an analytical expression giving all the approximately correct numerical values) is known. These conditions practically deprive his formulation of all its significance, because the first condition is not always met and the second cannot yet even be approximated. Even if both conditions can be met, the function  $N(q)$  obtained does not necessarily satisfy the equation  $\int_{-\infty}^{+\infty} N(q) dq = 1$ .

<sup>1</sup> R. Sips, *J. Chem. Phys.* **16**, 490 (1948).

## The Triple-Dipole Interaction between Atoms and Cohesion in Crystals of the Rare Gases

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October 3, 1949

THE application of third-order perturbation theory to the interaction of neutral atoms was reported<sup>1</sup> to result in an interaction between triplets of atoms. The term in the third-order interaction energy which depends on triplets of atoms is

$$W_0''' = \sum_{j \neq 0} \sum_{\substack{k \neq 0 \\ k \neq j}} \frac{H_{0j} H_{jk} H_{k0}}{(W_j - W_0)(W_k - W_0)} \quad (1)$$

where  $W_j$ ,  $W_k$ , and  $W_0$  are the unperturbed energies of the intermediate states  $j$  and  $k$ , and the ground state, respectively.  $H_{0j}$  etc. are the matrix elements of the perturbation. If the perturbing potential is limited to the dipole-dipole term, the following approximate expression, called the triple-dipole interaction, is obtained for  $W_0'''$ .

$$W_0''' \approx \frac{3}{2} \frac{(V_1 + V_2 + V_3) V_1 V_2 V_3 \alpha_1 \alpha_2 \alpha_3 (3 \cos \gamma_1 \cos \gamma_2 \cos \gamma_3 + 1)}{(V_1 + V_2)(V_2 + V_3)(V_1 + V_3) R_{12}^3 R_{23}^3 R_{13}^3} \quad (2)$$

$V_1$ ,  $V_2$ , and  $V_3$  are the ionization potentials and  $\alpha_1$ ,  $\alpha_2$ , and  $\alpha_3$  the polarizabilities of the three atoms;  $R_{12}$ ,  $R_{23}$ , and  $R_{13}$  are the sides and  $\gamma_1$ ,  $\gamma_2$ , and  $\gamma_3$  the angles of the triangle formed by the nuclei of the atoms. For like atoms (2) becomes<sup>2</sup>

$$W_0''' \approx \frac{9}{16} \frac{V \alpha^3 (3 \cos \gamma_1 \cos \gamma_2 \cos \gamma_3 + 1)}{R_{12}^3 R_{23}^3 R_{13}^3} \quad (2a)$$

The triple-dipole interaction  $W_0'''$  is positive, i.e., repulsive, for all acute triangles and negative for most obtuse triangles.

It can be shown that  $W_0'''$  for three rare gas atoms is about one percent of the dipole-dipole interaction energy of the London type.<sup>3</sup> Since  $W_0'''$  is relatively small, it does not appear likely to contribute much to the cohesive energy even for molecular crystals. The dependence of  $W_0'''$  on the configuration of three atoms, however, suggested that the structure of the rare gas solids might be explained by the triple-dipole interaction. Argon, neon, krypton, and xenon crystallize in the face-centered-cubic lattice, one of the two closest-packed structures,<sup>4</sup> the other being the hexagonal-closest-packed lattice. London<sup>5</sup> showed that, assuming pairwise

additivity, the dipole-dipole interaction accounted largely for the cohesion of molecular crystals. However, the lattice sums of the dipole-dipole interaction for the f.c.c.<sup>6</sup> and h.c.p.<sup>7</sup> lattices do not differ by more than 0.01 percent. This is also true if the dipole-quadrupole or higher pole interactions are similarly summed, so the stability of the f.c.c. compared to the h.c.p. structure cannot be explained by differences in these interactions.

The triple-dipole interaction,  $W_0'''$ , was directly summed in both the f.c.c. and h.c.p. lattices for a cylindrical region whose radius and semi-altitude were about three times the nearest-neighbor distance. These calculations were made on IBM punched-card machines.<sup>8</sup>

For the above region the sum of  $W_0'''/K$ , where  $K$  equals  $\frac{1}{18} V \alpha^3 / r_0^3$ , is 56.686 for the f.c.c. and 56.727 for the h.c.p. lattice. From an examination of partial sums it seems that: (a)  $W_0'''/K$  converges to a value close to 57 and (b) the sum of  $W_0'''/K$  is roughly 0.04 greater for the h.c.p. compared to the f.c.c. lattice.

The triple-dipole interaction was computed for crystals of the rare gases using accepted values of  $V$ ,  $r_0$ , and  $\alpha$ , and 56.69 for the sum of  $W_0'''/K$ . From the results of Table I it is noted that the

TABLE I. Triple-dipole interaction for crystals of rare gases.

Element	Lattice sum of $W_0'''$ (repulsion) kcal./mole	Heat of sublimation kcal./mole
Neon	0.0090	0.51
Argon	0.093	1.86
Krypton	0.229	2.57
Xenon	0.335	3.59

triple-dipole interaction amounts to two to nine percent of the cohesive energy for most rare gas solids.

It seems unlikely that the difference in the triple-dipole interaction for the f.c.c. compared to the h.c.p. lattice, a difference less than a ten-thousandth of the cohesive energy, can explain the stability of the f.c.c. lattice for the rare gas elements. Details of this work will be published later.

<sup>1</sup> B. M. Axilrod and E. Teller, *J. Chem. Phys.* **11**, 299 (1943).

<sup>2</sup> The equation for  $W_0'''$  in reference 1 was incomplete in that the factor  $\frac{1}{18}$  had not been determined. In March, 1948, a letter was received from Mr. Yosio Muto of Japan who had also worked out the triple-dipole interaction. Mr. Muto's result for  $W_0'''$  appeared to be in agreement with (2a).

<sup>3</sup> The dipole-dipole interaction energy is approximately  $-\frac{1}{2}(V \alpha^2 / R^4)$  for like atoms.

<sup>4</sup> *Handbook of Chemistry and Physics* (1945).

<sup>5</sup> F. London, *Trans. Faraday Soc.*, **32**, 8 (1937).

<sup>6</sup> Lennard-Jones, *Proc. Roy. Soc.*, **A107**, 636 (1935).

<sup>7</sup> M. Goeppert-Mayer and G. Kane, *J. Chem. Phys.* **8**, 642 (1940).

<sup>8</sup> These calculations were made by the Computation Laboratory of the National Bureau of Standards, New York City, under sponsorship of the ONR.

## The Sodium (<sup>2</sup>P) Photo-Sensitized Decomposition of Ethane\*

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October 19, 1949

THE excitation energy of the sodium (<sup>2</sup>P) states is approximately 48.3 kcal.; the heat of formation of gaseous sodium hydride from the atoms is in the range 47<sup>1</sup> to 51.6<sup>2</sup> kcal. It might be expected, therefore, that, provided sodium hydride were formed, Na(<sup>2</sup>P) atoms could sensitize the decomposition of hydrocarbons having C—H bond strengths not exceeding 95.3 to 99.9 kcal. The analogous reaction is known to occur with Cd(<sup>3</sup>P<sub>1</sub>) atoms,<sup>3</sup> for which the excitation energy is 82.9 kcal. and the heat of formation of the hydride is 15.6 kcal.; in this case cadmium hydride bands were detected by resonance fluorescence.<sup>4</sup> Jungers and Taylor<sup>5</sup> made an unsuccessful attempt to sensitize the polymerization of ethylene with Na(<sup>2</sup>P) atoms, but it seemed reasonable to assume that their negative result was, by analogy with the data on

$\text{Cd}(^3P_1)$  and the lower olefins,<sup>6</sup> due to the dissipation of the electronic energy of the excited atoms in the double bond.

We now wish to report that a sensitized decomposition of ethane cannot be accomplished with  $\text{Na}(^2P)$  atoms. A total of seventeen experiments were performed at temperatures ranging from 228° to 292° and with ethane pressures from 18 to 118 mm. The sodium was distilled into the cell under high vacuum conditions in order to remove as much hydrogen as possible. From the data of Norrish and Smith<sup>7</sup> the quenching efficiency of hydrogen is approximately 117 times that of ethane. Purified ethane was admitted at the required pressure, frozen with liquid air, and the cell sealed off. In this way the whole of the cell volume could be kept at the temperature of the furnace to avoid distillation of the sodium to a cold zone with a consequent decrease in its partial pressure. In some experiments the sodium Lab Arc was placed outside the furnace and the light was admitted through a window; in other experiments the emitting portion of the lamp was inserted into the furnace where it entered a Dewar-shaped cell to take full advantage of the light intensity. The  $D$  lines were sufficiently narrow to be almost completely absorbed by the sodium vapor in the cell. The duration of illumination varied from three to 120 hours, after which the cell was sealed to the analysis apparatus and the gas removed through a break-off valve.

In most of the experiments the hydrogen recovered amounted to about 1.5 percent or less. The only other product consisted of less than one percent of a fraction having a vapor pressure of 0.1 mm at  $-32^\circ\text{C}$ , but the same material was found without illumination, both in the presence and in the absence of sodium. It can be concluded, therefore, that no photo-sensitized decomposition occurred.

The values quoted for the C—H bond strength in ethane range from 96.8 to 98 kcal.<sup>8</sup> If the larger value for the heat of formation of sodium hydride is correct the reaction would be exothermic; for the smaller value it might be endothermic by as much as 2.7 kcal. scarcely enough to preclude reaction at the temperatures used. It can probably be concluded that a quenching process resulting in the formation of sodium hydride would involve a considerable activation energy.

Although, energetically, the dissociation of hydrogen by  $\text{Na}(^2P)$  atoms is less favorable than that of ethane, a number of experiments were performed with hydrogen-ethane mixtures. If atomic hydrogen had been produced, products such as methane would undoubtedly be formed. However, the results were again negative.

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<sup>1</sup> A. G. Gaydon, *Dissociation Energies* (Chapman and Hall, Ltd., London, 1947).

<sup>2</sup> F. R. Bichowsky and F. D. Rossini, *Thermochemistry of Chemical Substances* (Reinhold Publishing Corporation, New York, 1936).

<sup>3</sup> E. W. R. Steacie and R. Potvin, *J. Chem. Phys.* 7, 782 (1939).

<sup>4</sup> E. W. R. Steacie and D. J. LeRoy, *J. Chem. Phys.* 12, 34 (1944).

<sup>5</sup> J. C. Junger and H. S. Taylor, *J. Chem. Phys.* 4, 94 (1936).

<sup>6</sup> D. J. LeRoy and E. W. R. Steacie, *J. Chem. Phys.* 10, 683 (1942).

<sup>7</sup> R. G. W. Norrish and W. MacF. Smith, *Proc. Roy. Soc. (London)* A176, 295 (1940).

<sup>8</sup> E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1946).

## The Kinetics of the Pyrolysis of Allyl Bromide

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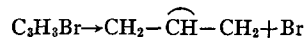
July 20, 1949

THERE are three main processes by which the pyrolysis of organic bromides may occur. First, a direct unimolecular split into HBr and an olefin as observed by Kistiakowsky and Stauffer<sup>1</sup> in the case of *tert.*-butyl bromide. Second, a breaking of the C—Br bond, leading to a bromine atom, which may further interact with the system leading to HBr and an olefin by a non-chain, radical mechanism. This behavior has been postulated by Daniels<sup>2-5</sup> and his co-workers in the case of ethyl bromide. Third, the bromine atom may participate in the propagation of

long chains. The behavior of methyl bromide, investigated by Meissner and Schumacher<sup>6</sup> is suggestive of such a mechanism. The case of allyl bromide is of particular interest, since the stability due to resonance of the allyl radical should facilitate the breaking of the C—Br bond.

Investigation has shown that essentially all the HBr is eliminated from allyl bromide and that the ratio of the final to initial pressure is about 1.5. The reaction is homogeneous and first-order rate constants calculated from both analytical and pressure results are in good agreement. However, it is found that as the initial pressure of allyl bromide is reduced below about 300 mm, the constants fall. Oxygen, nitrogen, and propylene have no influence on the rate, but hydrogen is capable of restoring the low pressure rate to its high pressure value.

In view of these observations it would appear that the pyrolysis of allyl bromide takes place by the initial step



and by a Lindemann mechanism. The rate constant in the range 320–380°C can be represented by the expression

$$k = 2.11 \times 10^{12} e^{-46,500/RT} \text{ sec.}^{-1}.$$

The Anhenius plot is shown in Fig. 1. Each point represents the

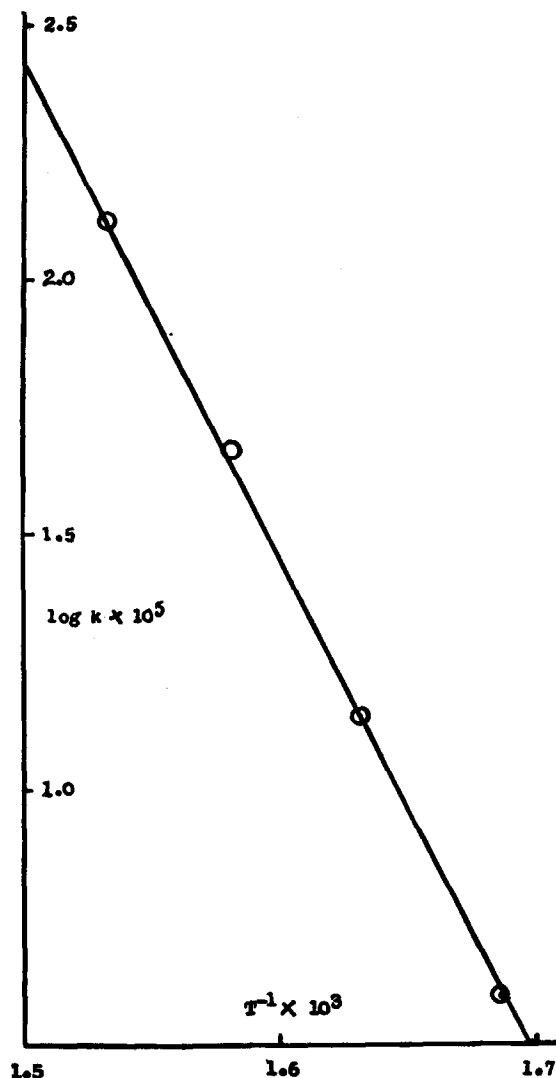


FIG. 1. Plot of  $\log K \times 10^5$  against  $1/T$ .