The Kinetics of the Pyrolysis of Allyl Bromide

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Cd($^3P_1$) and the lower olefins,[6] 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 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[7] 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°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.[8] 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 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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[1] A. G. Gaydon, *Dissociation Energies* (Chapman and Hall, Ltd., London, 1947).

[2] F. R. Bichowsky and F. D. Rossini, *Thermochemistry of Chemical Substances* (Reinhold Publishing Corporation, New York, 1936).

[3] E. W. R. Steacie and R. Potvin, J. Chem. Phys. **7**, 782 (1939).

[4] E. W. R. Steacie and D. J. LeRoy, J. Chem. Phys. **12**, 34 (1944).

[5] J. C. Jungers and H. S. Taylor, J. Chem. Phys. **4**, 94 (1936).

[6] D. J. LeRoy and E. W. R. Steacie, J. Chem. Phys. **10**, 683 (1942).

[7] R. G. W. Norrish and W. MacF. Smith, Proc. Roy. Soc. (London) **A176**, 295 (1940).

[8] E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1946).

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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[1] 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[2–5] 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[6] 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

$$C_3H_3Br \rightarrow CH_2-\overparen{CH}-CH_2+Br$$

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

$$k=2.11\times10^{12}e^{-45,500/RT}\ \text{sec.}^{-1}.$$

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

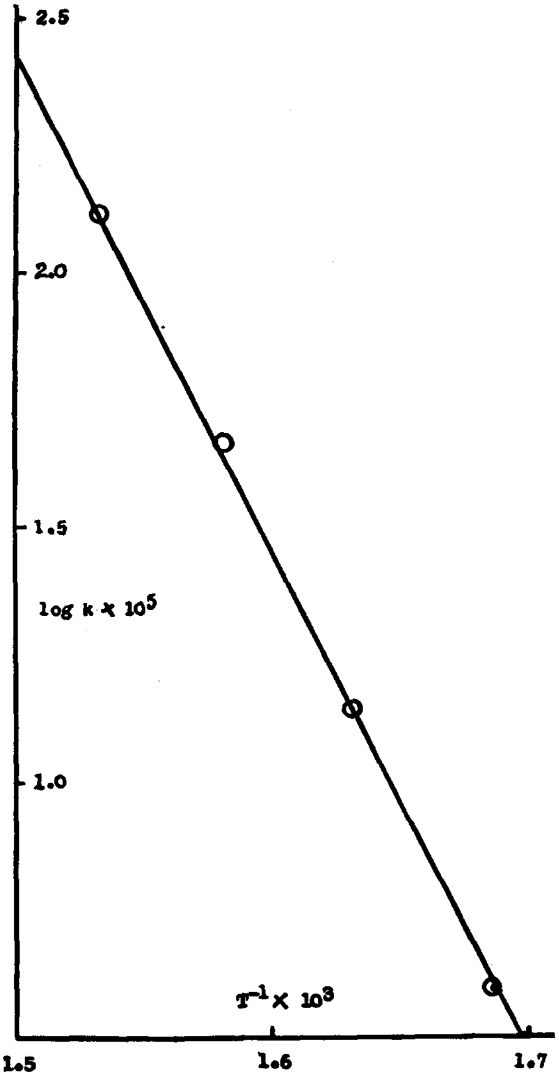

Fig. 1. Plot of log$K\times10^5$ against $1/T$.

mean of about six runs. The activation energy of the reaction, is in excellent agreement with the bond dissociation energy of C−Br in allyl bromide suggested by Roberts and Skinner.[7] This value is derived from a measurement of the heat of formation of allyl bromide, together with the heat of formation of the allyl radical as determined by Szwarc[8] from the pyrolysis of propylene.

Using the Bichowsky and Rossini[9] data for the heat of formation of CH_3Br and that of Kistiakowsky *et al.* for the C−H bond dissociation energy in CH_4, the value 67.3 kcal. may be arrived at for the C−Br bond dissociation energy in methyl bromide. The difference between the value for methyl bromide and that for allyl bromide is not directly comparable with the quantum-mechanical calculation of the resonance energy of the allyl radical, because of the neglect of the difference in the energies of reorganization of the two radicals.

A fuller account of this work will shortly be presented elsewhere.

[1] Kistiakowsky and Stauffer, J. Am. Chem. Soc. **59**, 165 (1937).
[2] Lessig, J. Phys. Chem. **36**, 2225 (1932).
[3] Vernon and Daniels, J. Am. Chem. Soc. **55**, 922 (1933).
[4] Fugani and Daniels, J. Am. Chem. Soc. **60**, 771 (1938).
[5] Daniels and Veltman, J. Chem. Phys. **7**, 756 (1939).
[6] Meissner and Schumacher, Zeits. f. physik. Chemie **185**, 435 (1940).
[7] Roberts and Skinner, Trans. Faraday Soc. **45**, 339 (1949).
[8] Szwarc, J. Chem. Phys. **17**, 284 (1949).
[9] Bichowsky and Rossini, *The Thermochemistry of Chemical Substances* (Reinhold Publishing Corporation, New York, 1936).

The Vibrational Spectra and Structure of the Aluminum Hydride Ion

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THE chemical and physical properties of lithium borohydride ($LiBH_4$) and lithium aluminum hydride ($LiAlH_4$) suggest the presence of the BH_4^- and AlH_4^- ions in their respective crystals.[1-3] In order to determine if the AlH_4^- ion exists in solution, the infra-red and Raman spectra of a 1.28 M solution of $LiAlH_4$ in diethyl ether have been studied. The sample of $LiAlH_4$ used in this work was obtained from the Metal Hydrides Corporation and had a purity of 96 percent. The transparent ether solution was prepared by refluxing the solid with anhydrous ether for several hours followed by decantation after the undissolved solid material had settled to the bottom of the container. Samples were pipetted under anhydrous conditions into Raman tubes and sealed before hydrolysis by atmospheric water vapor occurred. A similar procedure was used in filling the infra-red absorption cells.

The infra-red spectrum of the solution was obtained on a Beckman IR-2 infra-red spectrometer in the region 3μ to 15μ. The absorption peaks of the solute were obtained by subtracting the peaks due to the ether from those of the solution. By this procedure the infra-red spectrum was found to consist of two intense bands, with peaks at 764 and 1740 cm^{-1}. Both bands were broad. No weaker bands were observed although it is conceivable that some could be hidden under ether absorptions. The band at 1740 cm^{-1} has some asymmetry.

The Raman spectrum was obtained using a three-prism Zeiss instrument with a camera lens of aperture number 4.5. The plate factor at 4500A was 30A/mm. The excitation unit has been described elsewhere.[4] Its main features are six AH2 General Electric lamps, six elliptical reflectors, and a filter cell at the center of which is located a 5 ml Raman tube. The 4358A mercury line was used for excitation. The 4047A mercury line was removed using a filter solution of saturated sodium nitrite. Solutions of rhodamine 5D GN extra (0.01 g/l) and praseodymium chloride ($\frac{1}{10}$ saturated) were used through a thickness of 1 cm to cut down the continuum above 4358A. Several Raman spectra were taken on various samples before one sufficiently free of a continuum was obtained. On the best two plates exposure times of two hours were used. The Raman shifts of the solute were obtained by subtracting those due to ether from those of the solutions. The results are summarized in Table I. The reality of the 769-cm^{-1} line may be questioned because of its intensity and the continuum on the plate, but its coincidence with the broad infra-red band at 764 cm^{-1} suggests that it is real.

TABLE I. Raman and infra-red data and assignments for the aluminum hydride ion.

Raman	I	Infra-red	I	Assignment	Symmetry
769	(1)	764	(5)	ν_4	F_2
799	(2)			ν_2	E
1741	(2)	1740	(5)	ν_3	F_2
1790	(3)			ν_1	A_1

Although rigorous selection rules derived for gases do not necessarily hold for substances in solution, the four Raman and two infra-red bands observed and the coincidence of the infra-red bands with two Raman bands are consistent with a tetrahedral model for the AlH_4^- ion in solution. The broadness of the infra-red bands is probably due to the partial splitting of the triply degenerate modes of vibration by liquid forces.

Force constants for the stretching and bending vibrations of the AlH_4^- ion have been calculated using a simple valence force model.[5] The values calculated for k and $k\delta/e^2$ are, respectively, 1.89 and $0.126\cdot10^5$ dynes/cm. Since the valence force model involves two force constants, there are two independent relations between the four frequencies which may be used as checks on the model. Table II gives calculated and observed values for $\lambda_3^2+\lambda_4^2$ and $\nu_3\nu_4/\nu_1\nu_2$. The agreement is good for a simple valence force model, the percentage error being less than the corresponding error for a number of other tetrahedral molecules and ions.[5]

TABLE II. Calculated and observed values for $\lambda_3+\lambda_4$ and $\nu_3\nu_4/\nu_1\nu_2$ assuming a simple valence force potential.

	Observed	Calculated
$\lambda_3+\lambda_4$	$2.14\cdot10^5$ dynes/cm	$2.26\cdot10^5$ dynes/cm
$\frac{\nu_3\nu_4}{\nu_1\nu_2}$	0.93	0.88

[1] Schlesinger and Brown, J. Am. Chem. Soc. **62**, 3429 (1940).
[2] Fenholt, Bond, and Schlesinger, J. Am. Chem. Soc. **69**, 1199 (1947).
[3] Smith, Sci. Progress **35**, No. 139, 515 (1947).
[4] Harrison, Lord, and Loofbourow, *Practical Spectroscopy* (Prentice-Hall, Inc., New York, 1948).
[5] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 182.

A Note on Temperature and the Recombination Coefficient

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EQUATIONS of the type

$$\alpha=AT^r,$$

where α = recombination coefficient (cm/sec.),[1] T = temperature (°K), and A = dimensional constant have been postulated on many occasions. In early studies on air, carbon dioxide and hydrogen, Erikson[2,3] obtained values which indicate that the exponent $-2.5\leqslant r\leqslant-2.2$ when T varies from 90°K to 450°K. However, in Erikson's results, $A\neq$ constant. At about the same period Phillips experimentally found $r=-2.2$ for air at constant pressure in the temperature range from about 80°K to 500°K. At low pressures Thomson and Thomson[4] theoretically indicate that $r=-3$. On the