A more detailed account of the studies of the photolysis of the various amine-halomethanes will be separately reported by one of the present authors (G.M.C.). At this point we will note but one other observation on this photolysis, namely that the order of reactivity of the three tetrahalomethanes considered in the present paper increases in the order

$$FCCl_3 < ClCCl_3 < BrCCl_3,$$

and CBr_4 is even more reactive than $BrCCl_3$ as might be expected.

Finally, it should be noted that to the extent that we associate charge transfer character with the absorption bands of these amine–halomethane complexes, it is not appropriate to describe their spectral location in terms of a red shift from the $n \rightarrow \sigma^*$ band of the amine. The absorption band is a new one, characteristic of neither of the components of the complex.[13] However, the spectral location of the absorption band of the complex should be related to the difference between the ionization potential of the base component and the electron affinity of the "acid" component.[11,14] If we accept the result shown in Table I, the essential equality of the constants for formation of the complexes of triethylamine with each of the halomethanes, then the $K\epsilon_c$ curves become essentially ϵ_c curves for the complexes. No relation between red shift and electron affinity is revealed in the results.

[13] A. B. F. Duncan, "Annual Reviews of Phys. Chem.," Vol. V, Stanford, California, 1954, pages 185–194.

[14] H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

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The Effect of Pressure on the Rate and Equilibrium Constants of Chemical Reactions. The Calculation of Activation Volumes by Application of the Tait Equation[1]

BY SIDNEY W. BENSON AND JEROME A. BERSON

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By a detailed analysis of the effect of pressure changes on rate and equilibrium constants, it is shown that the usual assumption that the volume change or volume of activation is independent of pressure is seriously in error. An explicit expression for the pressure-dependence of the above constants in non-ionic systems is derived by use of the Tait Equation. With this expression, it is possible to evaluate independently the volume of activation at zero pressure and the coefficient of compressibility of the transition state. In addition, a simple analytical procedure is developed for obtaining the Tait constants from P*-V*-T data. For ionic systems, corrections for the pressure-dependence of the activity coefficients are shown to be negligible in water solution but important in systems of lower dielectric constant. The most important effects in ionic systems arise from the electrostriction of the solvent, and these can overshadow the normal compressibility effects. An explicit analysis of ionic systems involves a knowledge of ionic sizes; further, the pressure-dependences of both the activity coefficient and electrostriction terms are different from that of the short-range molar volume term. It is therefore doubtful that the data for ionic systems can be uniquely interpreted. Data from the literature on the rates of decomposition of azo-bis-isobutyronitrile and the Diels–Alder dimerization of isoprene are re-examined and shown to yield interpretations quite different from those of the original authors. Attention is called to the importance of adiabatic heating and temperature gradients in producing significant errors in the study of the pressure-dependence of reaction rates.

The interpretation of reaction rates by the transition state theory, involving thermodynamic treatment of activation parameters, implies the concept of an activation volume.[2–4] For a reaction $aA + bB + \cdots \rightleftarrows X^{\ddagger} \rightarrow$ Product in solution, the rate constant k is given by

$$k = \frac{RT}{Nh} K^{\ddagger} \frac{\gamma_A \gamma_B}{\gamma_x^{\ddagger}} = \frac{RT}{Nh} K^{\ddagger} K_\gamma \qquad (1)$$

where $K^{\ddagger}$ is the thermodynamic equilibrium constant at infinite dilution for the conversion of the reactants to the transition state $X^{\ddagger}$, and the γ's are activity coefficients of the species in question. The pressure-dependence of the rate constant is

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = \left(\frac{\partial \ln K^{\ddagger}}{\partial P}\right)_T + \left(\frac{\partial \ln K_\gamma}{\partial P}\right)_T \qquad (2)$$

By substituting $\ln K^{\ddagger} = -\Delta F^{\ddagger}/RT$ and using the thermodynamic relationship $(\partial F/\partial P)_T = V$, we can convert equation 2 to

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = \frac{-\Delta V^{\ddagger}}{RT} + \left(\frac{\partial \ln K_\gamma}{\partial P}\right)_T \qquad (3)$$

$\Delta V^{\ddagger}$ and $\Delta F^{\ddagger}$ represent the change in partial molar quantities; $\Delta V^{\ddagger}$ is the difference in partial molar volume $(V_t - \Sigma V_r)$ between the transition state and the reactants, and $\Delta F^{\ddagger}$ is the corresponding difference in standard partial molar free energies. The interpretation of the pressure-dependence of the reaction rate constant (or equilibrium constant, which is expressible by the same formalism) requires the separate evaluation of both $\Delta V^{\ddagger}$ and $(\partial \ln K\gamma/\partial P)_T$. The present paper offers an explicit solution to this problem.

The Contribution of Ionic Activity Coefficient Effects to the Pressure-dependence of Rates and Equilibria.—According to the Debye–Hückel limiting law,[5a] the molal activity coefficient of an

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[1] One of the authors (SWB) is indebted to the U. S. Atomic Energy Commission for a grant in support of his efforts on this project. The contributions of the co-author (JAB) were supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[2] M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935).

[3] (a) *Cf.* S. D. Hamann, "Physico-Chemical Effects of Pressure," Academic Press, Inc., New York, N. Y., 1957, Chapter 9. (b) *Ibid.*, pp. 54-57.

[4] *Cf.* S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp. 510–518.

[5] *Cf.* (a) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Company, Inc., New York, N. Y., 1958, pp. 164–170. (b) Ref. 4, pp. 521–528,

ion in very dilute solution is given by

$$\ln \gamma_i = -z_i^2 A\mu^{1/2} \qquad (4)$$

where z_i is the ionic charge number, μ is the ionic strength and A is a parameter which varies as $1/D^{3/2}T^{3/2}$, D being the dielectric constant of the solution. For 1:1 electrolytes in aqueous solution at 25°, A has the value[5a] 0.51 $1.^{1/2}$ $\text{mole}^{-1/2}$. When two or more ions (L^{z_l}, M^{z_m}, ...), each of charge z_i, react to form a transition state $(L.M...)^{z_l + z_m + \cdots}$, the activity coefficient ratio can be expressed as

$$\ln \frac{\gamma_{lm\ldots}}{\gamma_l \gamma_m} = -\ln K_\gamma = -A\mu^{1/2}\,[(z_l + z_m + \ldots)^2 - z_l^2 - z_m^2 - \ldots] = -2A\mu^{1/2}\sum_{i>j} z_i z_j \qquad (5)$$

The pressure-dependence of K_γ is then (neglecting the effect of small volume changes on μ)

$$\left(\frac{\partial \ln K_\gamma}{\partial P}\right)_T = 2\mu^{1/2}\sum_{i>j} z_i z_j \left(\frac{\partial A}{\partial P}\right)_T = 2A\left(\frac{\partial \ln A}{\partial P}\right)_T \mu^{1/2}\sum_{i>j} z_i z_j$$
$$= (\ln K_\gamma)(\partial \ln A/\partial P)_T$$
$$= 1.02\left(\frac{\partial \ln A}{\partial P}\right)_T \mu^{1/2}\sum_{i>j} z_i z_j \qquad (6)$$

Using equations 7 and 8, we may convert 6 to 9

$$\Delta V_\gamma{\ddagger} = -RT\left(\frac{\partial \ln K_\gamma}{\partial P}\right)_T \qquad (7)$$

$$\left(\frac{\partial \ln A}{\partial P}\right)_T = -\frac{3}{2}\left(\frac{\partial \ln D}{\partial P}\right)_T \qquad (8)$$

$$\Delta V_\gamma{\ddagger} = \frac{3}{2} RT \ln K_\gamma \left(\frac{\partial \ln D}{\partial P}\right)_T$$
$$= 1.53\, RT\mu^{1/2}\left(\frac{\partial \ln D}{\partial P}\right)_T \sum_{i>j} z_i z_j \qquad (9)$$

The differential term of equation 9 may be evaluated numerically from the empirical Owen–Brinkley equation[6]; for water it has the value 5.9 × 10^{-5} atm.^{-1} at 1 atm. For the reaction of two ions each of unit charge in aqueous solution at 25° at a concentration of 0.01 M, the contribution ($\Delta V_\gamma{\ddagger}$) of the pressure-dependence of the activity coefficient to the over-all volume of activation is thus about 0.2 cc./mole. Even for reactions of doubly-charged ions, $\Delta V_\gamma{\ddagger}$ is still less than 1 cc./mole. Activity coefficient effects on volumes of activation in water thus can be neglected in discussions of all but the least pressure-sensitive reaction rates. At higher ionic strength the simple Debye–Hückel treatment breaks down and other empirical relations must be used. In solvents of lower dielectric constant such as alcohols or acetone, these effects can be quite important, since the A parameter can be 10-fold larger and the coefficient $(\partial \ln D/\partial P)_T$ is also larger. In such cases the effects can be computed using equations 4 and 6 together with the proper values of A. It is important to note however, that in any case the pressure-dependence of $\Delta V_\gamma{\ddagger}$ does not fit the relation given later (eq. 25) for the non-ionic systems but must be evaluated with an additional term which can be obtained from equation 25.

Electrostrictive Effects.—The parameter $\Delta V{\ddagger}$ of equation 3 may be looked upon as a composite quantity, being made up of effects on the volume due to short-range changes in packing and geometry and effects due to changes in long-range forces between solute and solvent.[2] No precise separation of this type may be made in general. However the use of a specific model for solute-solvent interactions does permit such a separation. In ionic systems the long-range effects can be rather large. This arises from the rather large changes in electrostriction which occur in ionic solutions. For simple 1–1 electrolytes such as NaCl, KCl, etc. the partial molar volumes of the ions in aqueous solution are about 10 cc./mole smaller than the molar volumes of either the solid salts or the extrapolated values of the super-cooled, molten salts. In non-aqueous systems of lower dielectric constant and/or higher compressibility, these electrostriction volumes can be factors of 2 to 4 times larger. These rather substantial volume changes can be accounted for semi-quantitatively[7,8] in terms of the simple Born model for solvation and can be looked upon as an electrostriction of the solvent due to the ion-solute interactions.

The electrostriction volume V_e from the Born model is given in terms of the crystal radius of the ion r_i and the dielectric constant D of the solvent.

$$V_e = \left(\frac{\partial F_e}{\partial P}\right)_T = \frac{-\epsilon_i^2}{2r_i D}\left(\frac{\partial \ln D}{\partial P}\right)_T \qquad (10)$$

It has the value[8] of about 6 cc./Å. for water solutions at 25° and is negative in sign. It decreases in magnitude with increasing pressure, the net effect being to make the partial molar volumes of electrolytes increase with increasing pressure. The contribution to $RT \ln K$ of changes in V_e with pressure is then merely the difference in free energy of solvation with pressure

$$\int_0^P V_e \mathrm{d}P = \int_0^P \left(\frac{\partial F_e}{\partial P}\right)_T \mathrm{d}P = \frac{\epsilon_i^2}{2r_i}\left(\frac{1}{D} - \frac{1}{D_0}\right) = \frac{-\epsilon_i^2}{2r_i D_0}\left(1 - \frac{D_0}{D}\right) \qquad (11)$$

where $D - D_0$ represents the effective change in D between pressure P and reference pressure $P = 0$. In water solutions at 25°, the change in V_e can be as much as 50% over a 3000 atmosphere change in pressure. In non-aqueous systems of lower dielectric constant the effects can be much larger. The principal contribution to such effects can be interpreted[8] as arising from the changes with pressure of the coefficient of compressibility of the solvent, the latter in turn causing increases in D.

For most liquids the variation in dielectric constant with volume is approximately linear on a log–log plot[8] so that equation 11 can be recast in terms of the volume as

$$\Delta F_e = \int_0^P V_e \mathrm{d}P \sim -\frac{\epsilon_i^2}{2r_i D_0}\left[1 - \left(\frac{V}{V_0}\right)^\theta\right] \qquad (12)$$

where θ is a constant nearly independent of temperature and close to 1.4 for many polar liquids. Since volume changes for many liquids are small compared to V_0, even over a range of 10,000 atmos-

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[6] Ref. 5, p. 162.

[7] P. Mukerjee, *J. Phys. Chem.*, **65**, 744 (1961).

[8] S. W. Benson, unpublished work. The contribution of the term $\partial(1/r)/\partial p$ is negligible.

pheres, we can write

$$\left(\frac{V}{V_0}\right)^{\theta} = \left(\frac{V_0 - \Delta V}{V_0}\right)^{\theta} = \left(1 - \frac{\Delta V}{V_0}\right)^{\theta} \sim 1 - \theta\left(\frac{\Delta V}{V_0}\right) \qquad (13)$$

so that to this order of approximation equation 12 becomes

$$\Delta F_e \sim -\frac{\epsilon_i{}^2\theta}{2r_iD_0}\left(\frac{\Delta V}{V_0}\right) \qquad (14)$$

The total contribution of electrostrictive effects to the pressure-dependence of the equilibrium constant for the ionic system $L^{z_l} + M^{z_m} + \ldots \rightleftarrows (L.M.\ldots)^{z_l + z_m + \cdots}$ is:

$$\Delta F_e = -\left(\frac{\Delta V}{V_0}\right)\frac{\theta\epsilon^2}{2D_0}\left[\frac{(z_l + z_m + \ldots)^2}{r_{\ddagger}} - \frac{z_l{}^2}{r_l} - \frac{z_m{}^2}{r_m} - \ldots\right] \qquad (15)$$

As we shall see later, the explicit pressure dependence of the term $(\Delta V/V_0)$ can be represented by the Tait equation for the solution. The term in brackets, however, requires an explicit knowledge of $r_{\ddagger}$, the equivalent radius of the transition state complex. While this may be approximated by $(r_l{}^3 + r_m{}^3 + \ldots)^{1/3}$ which is not very sensitive to the precise values of r_l and r_m, it is questionable if the Born model could apply well to a non-spherical transition state complex in which the local charge distribution and local dielectric constant are quite different from that for the initial ions L^{z_l}, M^{z_m}, etc.

For these reasons and the lack of sufficient experimental data to test the relation, we shall not pursue further the analysis of electrostrictive effects. It must be pointed out, however, that they are expected to be overwhelmingly large in non-aqueous systems and as will be seen later, will have a different kind of pressure dependence than the short range effects to be encountered in non-ionic systems.

The Use of the Tait Equation for Representing Volume-Pressure Relations.—Restricting our attention now to non-ionic systems, we can recast equation 3 as

$$-RT\,(\partial \ln k/\partial P)_T = \Delta V^{\ddagger} = V_t - V_g \qquad V_g = \Sigma V_r \qquad (16)$$

In general, $\Delta V^{\ddagger}$ is not a constant with pressure (the log *k vs. P* plot is curved), and equation 16 is therefore not directly integrable. A procedure that has been followed frequently in discussion of the problem involves the determination of a quantity $\Delta V_0{}^{\ddagger}$, the volume of activation at "zero" external hydrostatic pressure, from the limiting slope (at one atmosphere) of the log *k vs. P* plot. This is esthetically reproachable in that a large part of the data are disregarded. Moreover, embedded in the curvature of the log *k vs. P* plot is one of the important properties of the transition state, namely its compressibility. When only a fraction of the data is examined, a potential opportunity to extract this information is missed. In addition, it is in most cases experimentally difficult if not impossible to make the extrapolation to zero pressure, since the changes in rate constants over the range 0 to 1000 atmospheres are extremely small and the errors of measurement of the changes are very large. It appeared desirable to us to develop precise expressions for the pressure-dependence of $\Delta V^{\ddagger}$, which would permit equation 16 to be cast in integrable form and would open the entire pressure range to scrutiny.

The isothermal compressibilities of a number of liquids are correlated remarkably well[9,10] by an empirical equation 17 developed by Tait.[11] In equation 17, V_0 and V_p are volumes of liquid.

$$\kappa = \frac{V_0 - V_p}{V_0} = C \log\left(1 + \frac{B}{P}\right) \qquad (17)$$

at atmospheric pressure and at pressure P respectively, and C and B are positive constants. We have now checked the applicability of equation 17 to the compressibility data for several additional liquids. The data are taken largely from Bridgman's results[12] and are well fitted by equation 17. Rapid estimates for the constants of the Tait equation may be made by the following procedure.

TABLE I

SUMMARY OF GRAPHICALLY DETERMINED CONSTANTS OF THE TAIT EQUATION

Compound	Temp., °C.	B, kg./cm.²	C
n-Pentane	0	595	0.226
	50	315	.215
	95	160	.208
2-Methylpentane	0	630	.210
	50	380	.206
	95	245	.210
3-Methylpentane	50	370	.204
	95	255	.210
n-Heptane	50	430	.197
	95	355	.216
Isoprene	0	780	.220
	60[a]	330	.226
	75[a]	355	.252
n-Propyl chloride	0	890	.227
	50	475	.212
n-Propyl bromide	0	1085	.229
	50	725	.224
	95	515	.229
n-Propyl iodide	0	1340	.235
	50	1040	.237
	95	575	.224
n-Butyl chloride	0	1000	.223
	50	665	.221
n-Butyl bromide	0	1160	.226
	50	710	.217
n-Butyl iodide	0	1420	.235
	50	1020	.231

[a] Taken from the data of J. Peisach, Dissertation, Columbia University, 1958.

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(9) (a) R. E. Gibson and O. H. Loeffler, *Ann. N. Y. Acad. Sci.*, **51**, 727 (1949); (b) *J. Phys. Chem.*, **43**, 207 (1939).

(10) W. G. Cutler, R. H. McMickle, W. Webb and R. W. Schiessler, *J. Chem. Phys.*, **29**, 727 (1958).

(11) P. G. Tait, "Report on Some of the Physical Properties of Fresh-water and of Sea-water," from "Physics and Chemistry" of the voyage of H.M.S. Challenger, Vol. II, 1888, Part IV, *cf.* H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958, p. 379.

(12) *Cf.* Landolt-Börnstein, "Physikalisch-Chemische Tabellen," edited by W. A. Roth and K. Scheel, Springer Verlag, Berlin, 1923, p. 94 and supplements 1, 2 and 3.

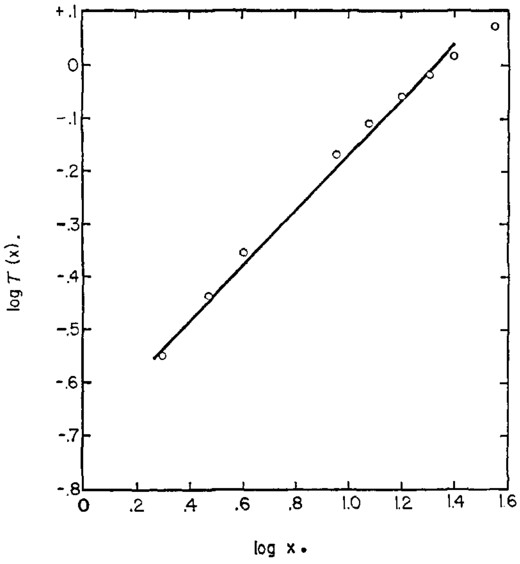

Fig. 1.

The ratio of the bulk compressions, κ_1/κ_2, at any two pressures P_1 and P_2 is given by

$$\frac{\kappa_1}{\kappa_2} = \frac{[\log (B + P_1) - \log B]}{[\log (B + P_2) - \log B]} \quad (18)$$

If $\kappa_1/\kappa_2 = 2$, equation 18 may be solved readily for B.

$$B = \frac{P_2^2}{P_1 - 2P_2};\ \kappa_1/\kappa_2 = 2 \quad (19)$$

From smoothed plots of the data (κ *vs.* log P)., well separated values are chosen such that $\kappa_1/\kappa_2 = 2$; B and C then are calculated from equations 19 and 17, respectively. Table I lists a set of Tait constants determined in this way. It is noteworthy that, although the values are fairly rough estimates as a result of having been determined graphically, C is essentially invariant with temperature for a given liquid, a feature previously noted[9,10] in other cases. Further, C is quite insensitive to structure. The average value for C from Table I is 0.214 ± 0.008. This corresponds very well to values of 0.216 and 0.205 previously reported[9,10] for other series of liquids.

Adopting the point of view of transition state theory, which ascribes molecular properties to the activated complex, we assume that the Tait equation expresses the compressibility of the activated complex as well as it does that of the reactants. Equations 16 and 17 can then be combined to give

$$-RT\left(\frac{\partial \ln k}{\partial P}\right)_T = (V_t^0 - V_g^0) - \frac{CV_t^0}{2.3}\ln\left(1 + \frac{P}{B_t}\right) + \frac{CV_g^0}{2.3}\ln\left(1 + \frac{P}{B_g}\right) \quad (20)$$

where V_t^0 and V_g^0 represent partial molar volumes of the transition and ground states at one atmosphere, and B_t and B_g represent Tait constants. We assume that the Tait constant C is the same for both the ground and transition states and that it has the value 0.216, which approximates the experimentally determined values for most liquids except water.[9-11] In any case, as will become apparent, an accurate choice of a value for C is not crucial. Integration of (20) gives

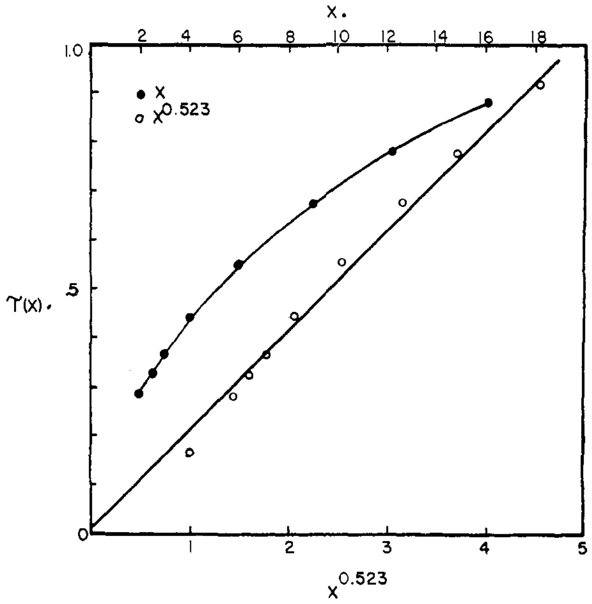

Fig. 2.

$$\frac{\log (k^p/k^0)}{P} = \frac{-\Delta V_0\mp}{2.3\ RT} - \frac{CV_g^0}{2.3\ RT}\left[\tau(x_g) - \frac{V_t^0}{V_g^0}\tau(x_t)\right]$$
$$= \frac{-\Delta V_0\mp}{2.3\ RT} - \frac{CV_g^0}{2.3\ RT}\psi \quad (21)$$

where

$$\tau(x) = \left(\frac{1}{x} + 1\right)\log(1 + x) - 0.4343 \quad (22)$$

and

$$x = P/B;\ \psi = \tau(x_g) - \frac{V_t^0}{V_g^0}\tau(x_t) \quad (23)$$

According to equation 21, if both the ground and transition states obey the Tait equation, a plot of log $(k^p/k^0)/P$ *vs.* ψ should be linear, with slope $-CV_g^0/2.3\ RT$ and intercept $-\Delta V_0\mp/2.3\ RT$. In order to plot the function ψ, however, it is necessary to know V_t^0 and B_t, neither of which is directly measurable. In principle, it would be possible to proceed by successive estimation of V_t^0 and B_t and insertion of the estimated values in (21), but this would involve a prohibitive amount of computational labor. The problem is simplified by a mathematical device in which $\tau(x)$ is approximated by an exponential function (24) of x.

$$\tau(x) \approx \sigma x^n + Q \quad (24)$$

A plot of log $\tau(x)$ *vs.* log x (Fig. 1) is nearly linear in the range of $0.3 < \log x < 1.5$, and the slope and intercept of the best straight line drawn through the points give estimates of n and σ in equation 24. Using the value (0.523) of n thus estimated, $\tau(x)$ is plotted against $x^{0.523}$ (Fig. 2) and is seen to be very nearly linear, with $Q = 0.008$ and $\sigma = 0.200$. In the range $2 < x < 16$, the true value of $\tau(x)$ does not deviate from that given by the linear plot by more than 4%, the average deviation being ±1.6%. Since the Tait constant B has values in the range 300–1000 kg./cm.^{2} for most liquids at ordinary temperatures, the range of x ($\equiv P/B$) 2 to 25 includes pressures from about 1000 to about 16,000 kg./cm.^{2}. This covers most of the pressure region that is both experimentally readily acces-

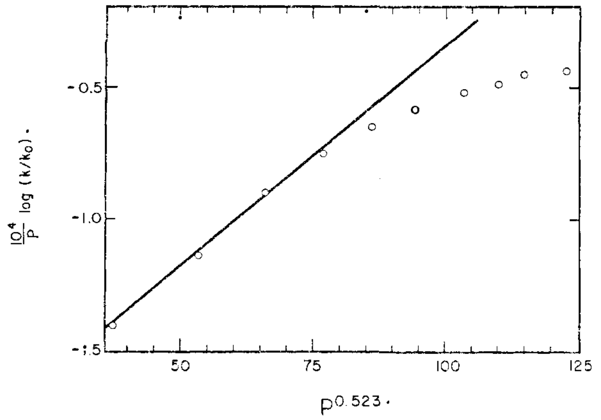

Fig. 3.—Decomposition of azo-bis-isobutyronitrile in solvent toluene in the presence of iodine at 62.5°.

sible and productive of significant changes in reaction rate. For most purposes then, $\tau(x)$ can be replaced by 0.200 $x^{0.523}$ + 0.008, and equation 21 reduces to

$$\frac{\log(k^{\mathrm{p}}/k^0)}{P} \approx \frac{-\Delta V_0^{\ddagger}}{2.3\,RT}(1 - 0.008C) - \frac{0.200CV_{\mathrm{g}}^0}{2.3\,RT}\left[\frac{1}{B_{\mathrm{g}}^{0.523}} - \left(1 + \frac{\Delta V_0^{\ddagger}}{V_{\mathrm{g}}^0}\right)\frac{1}{B_{\mathrm{t}}^{0.523}}\right]P^{0.523} \quad (25)$$

Thus, a plot of log $(k^{\mathrm{p}}/k^0)/P$ *vs.* $P^{0.523}$ should be linear, with slope and intercept equal numerically to the slope and intercept terms of equation 25. From the intercept (I) of such a plot, the activation volume at one atmosphere can be calculated, independent of the assignment of a numerical value to the Tait constant B_{t}. As equation 26 shows, the Tait constant C enters only as a small correction term; consequently, the assumption that C is the same for the ground and transition states cannot produce any substantial error in $\Delta V_0^{\ddagger}$. With the value of $\Delta V_0^{\ddagger}$ known, B_{t} then can be calculated

$$-\Delta V_0^{\ddagger} = \frac{2.3\,RTI}{1 - 0.008C} \quad (26)$$

by equating the slope of the $P^{0.523}$ plot to the slope term of equation 25, using the experimental values of B_{g} and V_{g}. The values of $\Delta V_0^{\ddagger}$ and B_{t} thus estimated may then be checked against the analytical expression 21 by insertion. The labor involved in this process is reduced by the use of large scale plots of x *vs.* $\tau(x)$ from Table II, in which for convenience, values of $\tau(x)$ as a function of x are collected.

The Pressure-dependence of the Reaction Rate for Some Non-ionic Systems.—For reactions of uncharged species in non-polar media, equation 25 should be followed. Unfortunately, the literature contains but few data for systems of the appropriate kind that are extensive enough to provide a real test. In Figs. 3 and 4 we have plotted $\log(k^{\mathrm{p}}/k^0)/P$ *vs.* $P^{0.523}$ for the decomposition of azo-bis-isobutyronitrile in solvent toluene in the presence of iodine at 62.5° (from the data of Ewald[13]) and for the Diels–Alder dimerization of isoprene in bulk at 60° and 75° (from the data of Walling and Peisach[14,15]).

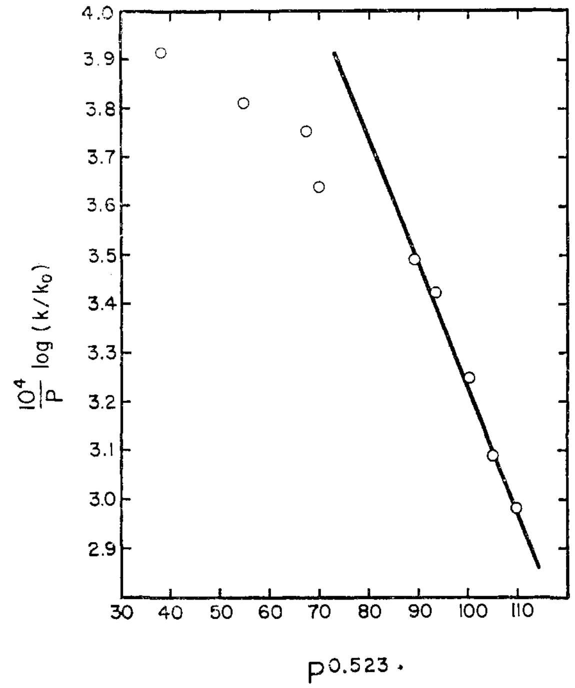

Fig. 4.—Diels–Alder dimerization of isoprene in bulk at 60°.

For the decomposition of azo-bis-isobutyronitrile (Fig. 3), the plot is nearly linear in the low-pressure region up to about 5000 atm. but becomes concave downward at higher pressures. The reasons for the failure of this system to obey equation 25 are not clear, but a possible complication may arise from the "cage effect.[16]" The value for $\Delta V_0^{\ddagger}$, + 12.4 cc./mole, calculated from the intercept of the linear portion of Fig. 3 and equation 25, agrees only approximately with that calculated[13] (+ 9.4 cc./mole) from the limiting slope of the log (k^{p}/k^0) *vs.* P plot. Since compressibility data for the azonitrile are not reported,[13] B_{g} is not available and B_{t} cannot be calculated.

TABLE II

VALUES OF $\tau(x)$ AS A FUNCTION OF $x^{0.523}$

x	$x^{0.523}$	$\tau(x)$
1.00	1	0.166
2.00	1.440	.281
2.50	1.615	.327
3.00	1.775	.366
4.00	2.06	.441
6.00	2.55	.552
9.00	3.15	.677
12.25	3.70	.775
16.00	4.26	.872
18.00	4.54	.915
20.25	4.84	.957
25.00	5.38	1.038
36.00	6.54	1.176

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(13) A. H. Ewald, *Discussions Faraday Soc.*, **22**, 138 (1956).

(14) C. Walling and J. Peisach, *J. Am. Chem. Soc.*, **80**, 5819 (1958).

(15) There appears to be an error in the data reported,[14] since the points for the runs at 60° and 4218 and 5132 kg./cm.[2] do not correspond in the log k *vs.* P plot to the figures given in tabular form. When re-plotted, these two points fall badly off a smooth curve of the other points and have therefore not been included in our computations.

(16) G. S. Hammond, C-H. S. Wu, O. D. Trapp, J. Warkentin and R. T. Keys, *J. Am. Chem. Soc.*, **82**, 5394 (1960), and references cited therein.

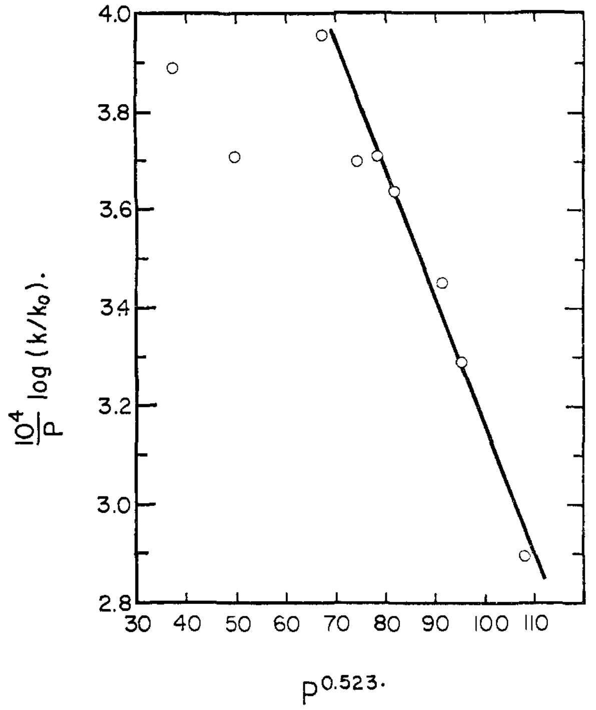

Fig. 5.—Diels-Alder dimerization of isoprene in bulk at 75°.

For the Diels–Alder dimerizations of isoprene at 60 and 75°, the plots (Figs. 4 and 5) are approximately linear in the range 4000–8000 kg./cm.^{2} but fall away from linearity at lower pressures. The 75° data are also badly scattered at low pressures, which presumably reflects the large uncertanity in the function log $(k^p/k^0)/P$ in this region. For example ±5% uncertainty in the rate constant k^p at 1019 kg./cm.^{2} $(P^{0.523} = 37.1)$ allows log $(k^p/k^0)/P$ to vary by as much as 12%. The uncertainty is much less serious in the high pressure range; log $(k^p/k^0)/P$ varies by less than 2% for ±5% uncertainty in k^p at 7593 kg./cm.^{2} $(P^{0.523} = 108)$. From the intercepts of the linear portions of Figs. 4 and 5, values of $\Delta V_0^{\ddagger}$ can be calculated from equation 26: at 75°, $\Delta V_0^{\ddagger} = -38.4$ cc./mole, and at 60°, $\Delta V_0^{\ddagger} = -36.5$ cc./mole. From these values, the known values of B_g, C and V_g, and equation 25, values for the Tait constants (B_t) of the transition state at 75 and 60° can be calculated. These are 530 and 525 kg./cm.^{2}, which are quite reasonable for a C_{10} hydrocarbon (see Table I). To check for consistency with the analytical equation 21, it is necessary to plot log $(k^p/k^0)/P$ vs. ψ. The latter function is extremely sensitive to small changes in the parameters $\Delta V_0^{\ddagger}$, B_g and B_t, so that compatibility is achieved with only minor adjustments of the approximate values calculated from equations 25 and 26. Figure 6 shows such a plot for the 60° data in which ψ is calculated from equation 23 using values of $\Delta V_0^{\ddagger}$ −36.5 cc./mole, $B_g = 300$ kg./cm.^{2} and $B_t = 525$ kg./cm.^{2}. The slope of the linear portion of the graph $(-7.5 \times 10^{-4}$ atm.$^{-1})$ is very close to the theoretical slope $(-7.6 \times 10^{-4}$ atm.$^{-1})$ calculated from the term $-CV_g^0/2.3\ RT$ of equation 21, and the intercept gives the value $\Delta V_0^{\ddagger} = -36.5$ cc./mole. These correspondences indicate compatibility of the linear portion with equation 21.

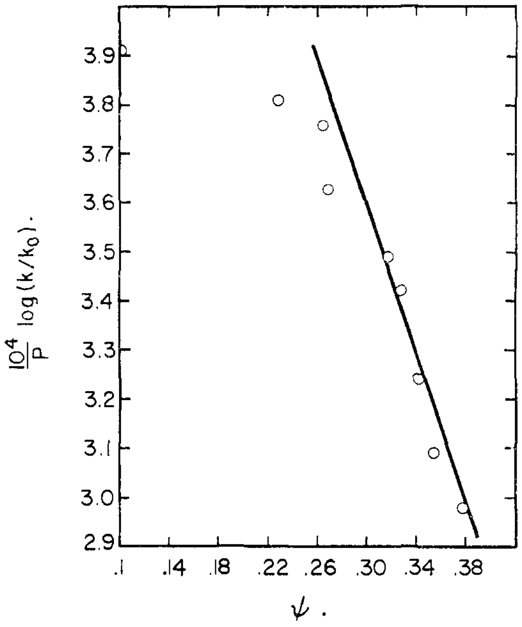

Fig. 6.—Diels-Alder dimerization of isoprene in bulk at 60°.

The present results are to be contrasted with those obtained[14] by calculating $\Delta V_0^{\ddagger}$ directly from the integrated form of equation 16 and the initial slope of the log (k^p/k_0) vs. P plot, on the assumption that $\Delta V^{\ddagger}$ is constant with pressure. This procedure gave[14] values of $\Delta V,^{\ddagger} = -25.6$ and −24.3 cc./mole at 75 and 60°. Although the plots of log (k^p/k^0) vs. P were approximately linear[14] in the range 0–3000 kg./cm.^{2}, the reasons for this are not obvious. Further, the log (k^p/k^0) vs. P plots were strongly curved[14] at pressures above 3000 kg./cm.^{2}.

The over-all volume changes for the conversion of two moles of isoprene to one of limonene were −48.7 and −45.5 cc./mole at 75 and 60°.[14] Since the values of $\Delta V_0^{\ddagger}$ calculated on the assumption that $\Delta V^{\ddagger}$ was constant were much smaller (by 21–23 cc./mole), Walling and Peisach concluded that the molar volume of the transition state must have been much larger than that of the product and that consequently, the transition state was a diradical involving the incipient formation of only one of the two diene-dienophile bonds. In our opinion, if one were to draw any mechanistic conclusion at all from the data, it would seem at least as reasonable to use the values obtained from the high-pressure linear portions of Figs. 4, 5 and 6, which put $\Delta V_0^{\ddagger}$ in the range −37 to −38 cc./mole. This would correspond to a transition state with a molar volume quite close to that of the final product and therefore presumably with *both* diene–dienophile bonds partially formed.[17]

One cannot ignore, however, the curvature at low pressures of the plots of Figs. 4, 5 and 6. This might indicate any of a number of disturbances, but the major source of concern is that the transi-

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(17) This of course does not exclude the possibility of an intermediate equilibrium state, in which one bond is made, followed by a rate determining cyclization to product.

tion state does not give evidence of obedience to the Tait equation over the entire pressure range. If the curvature is really caused by a departure of the transition state from a Tait-like response to pressure, the basis for inferring its "structure" or other "molecular" properties from the pressure-dependence of the rate is seriously undermined. We conclude, therefore, that inferences regarding the volume of activation for the dimerization of isoprene are unjustified.

It is unfortunate that there are so few reliable data on pressure effects in liquid systems. While the apparatus for such measurements is not very difficult to obtain, the measurements themselves are fraught with many errors. A very appreciable error can arise from the heating effects due to adiabatic compression. Thus some experimenters have reported thermal explosions in systems containing reactive dienes when the pressures were raised too rapidly. This heating occurs both in the reaction liquid and the hydraulic fluid. Since the thermal conductivities of liquids are rather small, it takes appreciable time to dissipate this heat and the rates must be corrected for the initially high temperatures. For reactions with usual activation energies such corrections can be considerable.

A second source of error arises from the heat liberated in exothermic reactions. Benson[18] has made an analysis of such errors and shown that in small vessels containing liquids the temperature error can be of the order of a few tenths °C. These errors are most pronounced for reactions having large heats of reaction and half-lives of the order of 1 hr. To date, very little attention has been given to these sources of error by workers in the field, but it appears to us that they can introduce considerable uncertainty in the data on pressure effects where small changes in rate are being measured.

(18) S. W. Benson, *J. Chem. Phys.*, **22**, 46 (1954).

[CONTRIBUTION FROM THE VENABLE LABORATORY, THE UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, N. C., AND THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF MISSISSIPPI, UNIVERSITY, MISS.]

Photochemical Interchange of Halogens in Aromatic Compounds. I[1a]

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The series of reactions, ArX + X′ → ArX′ + X, which are caused by light or peroxide–SO_2Cl_2, is discussed. Three new reactions of this type, the effects of some substituents on the rates of certain examples and the relative rates of displacement of bromine and iodine by a common reagent, chlorine, are reported.

Introduction

A number of investigators have reported that the side chain chlorination of the ring brominated toluenes proceeds anomalously,[2] with bromine appearing on the side chain and chlorine on the nucleus. Although Eibner's report, in 1903,[3] of the facile displacement of bromine from bromobenzene by chlorine clearly established that the methyl substituent is not required, Miller and Walling[4] were the first to report detailed further study of this simpler form of the displacement.

The experiments of Miller and Walling have demonstrated the intermediacy of halogen atoms in the reaction

$$Cl_2 + C_6H_5Br \xrightarrow{\text{light}} Br_2 + C_6H_5Cl$$

Because of the close analogy between displacement by a halogen atom and one by a free radical we are investigating in more detail this halogen displacement reaction and others closely related. Although the data now available are not extensive enough to shed light upon the nature of radical displacements on aromatic compounds, they have intrinsic interest.

Results

From consideration of the usual order of displacement in the halogen group, one might expect that a family of reactions analogous to the displacement of bromine from aromatic compounds by chlorine should be possible. In this family an halogen should be able to displace another of equal or higher atomic number

$$ArX + X' \longrightarrow ArX' + X$$
$$\text{at. no. } X' \leq \text{at. no. } X$$

giving rise to a total of ten reactions. Four of these involve fluorine and have not been investigated, but the remaining six have been observed. They are

$$ArCl + Cl^* \longrightarrow ArCl^* + Cl \qquad (A)$$
$$ArBr + Cl \longrightarrow ArCl + Br \qquad (B)$$
$$ArI + Cl \longrightarrow ArCl + I \qquad (C)$$
$$ArBr + Br^* \longrightarrow ArBr^* + Br \qquad (D)$$
$$ArI + Br \longrightarrow ArBr + I \qquad (E)$$
$$ArI + I^* \longrightarrow ArI^* + I \qquad (F)$$

Reaction B, of course, is well established, and reactions D and F have been reported by Miller and Walling[4] and by Noyes,[5] respectively. The remaining three reactions (A, C and E) are reported here for the first time.[6]

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(1) (a) Presented in part at the 138th National Meeting of the A.C.S., New York, N. Y., September, 1960. (b) To whom inquiries should be addressed, Department of Chemistry, The University of Mississippi.

(2) (a) O. Srpek, *Monatsh.*, **11**, 429 (1890); (b) S. C. J. Olivier, *Rec. trav. chim.*, **45**, 296 (1926); (c) F. Asinger, *Monatsh.*, **64**, 153 (1934); *J. prakt. Chem.*, **152**, 5 (1939); (d) G. L. Goerner and R. C. Nametz, *J. Am. Chem. Soc.*, **73**, 2940 (1951); (e) W. Voegtli, H. Muhr and P. Langer, *Helv. Chim. Acta*, **37**, 1627 (1954).

(3) A. Eibner, *Ber.*, **36**, 1229 (1903).

(4) B. Miller and C. Walling, *J. Am. Chem. Soc.*, **79**, 4187 (1957).

(5) R. M. Noyes, *ibid.*, **70**, 2614 (1948); R. M. Noyes and D. J. Sibbett, *ibid.*, **75**, 767 (1953).