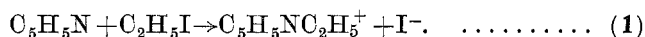


SHORT COMMUNICATIONS

A CRITIQUE OF THE VIEWS OF GONIKBERG AND POVKH ON THE ROLE OF SOLVATION IN A MENSCHUTKIN REACTION*

By S. D. HAMANN†

Pressure is known to have a marked effect on the rates of organic reactions in solution, and it is now apparent that many of the observed changes in rate arise from the enhanced solvation of electrically charged groups at high pressures (Buchanan and Hamann 1953 ; David and Hamann 1954 ; Burris and Laidler 1955). In principle, the pressure dependence of a reaction rate may be used to provide information about the relative extent of solvation in the initial and transition states of the reaction, but deductions of this sort must be made with great caution. To illustrate this point we shall examine the conclusions of Gonikberg and Povkh (1949) and Gonikberg (1955*a*, 1955*b*) concerning the role of solvation in the formation of *N*-ethyl pyridinium iodide from pyridine and ethyl iodide in acetone solution



Gonikberg and Povkh concluded from the high pressure kinetic measurements of Gibson, Fawcett, and Perrin (1935) that the transition state for reaction (1) is "unsolvated" in the sense that there is no electrostriction of the solvent in the neighbourhood of the incipient charges. This is a surprising conclusion, and one which contradicts a good deal of other evidence concerning the part played by solvents in the formation of quaternary ammonium salts (Menschutkin reactions). We shall review this evidence briefly, before considering the foundations of Gonikberg's argument. The experiments of Moelwyn-Hughes and Hinshelwood (1932) show that a Menschutkin reaction will not occur in the homogeneous gas phase ; it requires a solvent or an active surface to stabilize the transition state, and the rate of reaction is known to be roughly proportional to the dielectric constant of the solvent. Furthermore, reactions of this class have very negative entropies of activation : for example, the activation entropy for reaction (1) in acetone solution is $-35 \text{ cal deg}^{-1} \text{ mole}^{-1}$. This large decrease almost certainly represents the amount of entropy lost by the solvent molecules which are frozen around the partially ionic transition state (Bell 1943). The fact that the activation entropy is nearly the same as the total entropy decrease for the complete reaction shows that the transition state is almost as highly ionic and extensively solvated as the free ions (Glasstone, Laidler, and Eyring 1941).

* Manuscript received May 17, 1956.

† Division of Industrial Chemistry, C.S.I.R.O., High Pressure Laboratory, University of Sydney.

Turning now to an examination of Gonikberg's argument, we find that he made the reasonable assumption that the effective volume of the transition state for Menshutkin reactions is close to that of the final product. The justification for this lies in the fact that the rate of a reverse Menshutkin reaction is only slightly reduced by the pressure (Williams, Perrin, and Gibson 1936). On this basis the effective volume of activation ΔV^\ddagger , defined by

$$\Delta V^\ddagger = -RT \frac{\partial \ln k}{\partial P}, \quad \dots\dots\dots (2)$$

where k is the rate constant, should be almost equal to the difference $\Delta \bar{V}$ between the partial molar volumes of the products and reactants in the same solvent. Gonikberg and Povkh (1949) measured $\Delta \bar{V}$ for reaction (1) in acetone at 1 atm

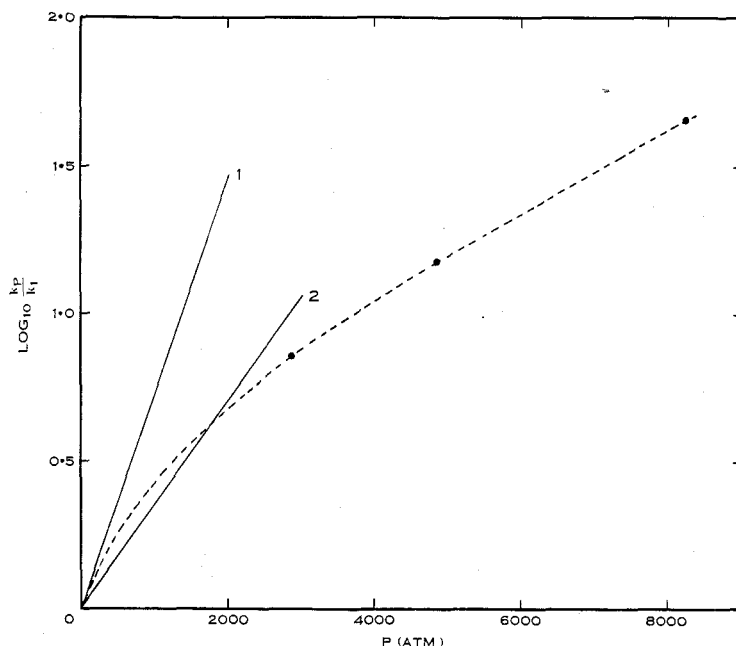


Fig. 1.—The rate of the reaction (1) at high pressures and at 30 °C.

and found it to be $-42 \text{ cm}^3 \text{ mole}^{-1}$, which is twice as great as the value $\Delta V^\ddagger = -20 \text{ cm}^3 \text{ mole}^{-1}$ at 1 atm, estimated by Stearn and Eyring (1941) from the kinetic measurements of Gibson, Fawcett, and Perrin (1935) at 1 and 2890 atm. Confronted with this discrepancy Gonikberg and Povkh then measured the molar volume of pure liquid *N*-ethyl pyridinium iodide and found it to be greater by $26 \text{ cm}^3 \text{ mole}^{-1}$ than the partial molar volume of the same substance in acetone solution. From this they concluded that the hypothetical reaction of pyridine with ethyl iodide in acetone to give pure liquid (unsolvated) *N*-ethyl pyridinium iodide would be accompanied by almost the same volume change as the activation step for the real reaction (1). This is the main basis of their conclusion that the transition state is not solvated.

The flaw in this argument lies in the authors' acceptance of Stearn and Eyring's value for ΔV^\ddagger at 1 atm. Figure 1 shows that the slope of the curve of $\log k$ against P changes very rapidly at low pressures, and without measurements below 2890 atm it is quite impossible to guess the limiting slope at 1 atm, and so derive ΔV^\ddagger from equation (2). The line 1 corresponds to the value $-42 \text{ cm}^3 \text{ mole}^{-1}$, and the line 2 to $\Delta V^\ddagger = -20 \text{ cm}^3 \text{ mole}^{-1}$: the dotted curve is one which was drawn arbitrarily by Williams, Perrin, and Gibson (1936). It is clear that Stearn and Eyring's choice of $-20 \text{ cm}^3 \text{ mole}^{-1}$ is no better, and probably worse than the value $-42 \text{ cm}^3 \text{ mole}^{-1}$ which is Gonikberg and Povkh's measured volume change for the formation of the solvated salt.

The difficulty of estimating volume changes at 1 atm from rate and equilibrium measurements at high pressures is emphasized by the following values for the difference between the partial molar volumes of piperidine in the ionized and un-ionized forms in methanol at 25 °C (Hamann and Strauss 1956):

P (atm)	1	50	250	750	1500	2500
$\Delta \bar{V}$ ($\text{cm}^3 \text{ mole}^{-1}$)	..	-49.5^*	-46^\dagger	-32^\dagger	-28^\dagger	-24^\dagger	-19^\dagger	

Obviously, any attempt to estimate $\Delta \bar{V}$ at 1 atm from measurements above 2500 atm would be doomed.

References

- BELL, R. P. (1943).—*J. Chem. Soc.* **1943**: 629.
 BUCHANAN, J., and HAMANN, S. D. (1953).—*Trans. Faraday Soc.* **49**: 1425.
 BURRIS, C. T., and LAIDLER, K. J. (1955).—*Trans. Faraday Soc.* **51**: 1497.
 DAVID, H. G., and HAMANN, S. D. (1954).—*Trans. Faraday Soc.* **50**: 1188.
 GIBSON, R. O., FAWCETT, E. W., and PERRIN, M. W. (1935).—*Proc. Roy. Soc. A* **150**: 223.
 GLASSTONE, S., LAIDLER, K. J., and EYRING, H. (1941).—"The Theory of Rate Processes." p. 418. (McGraw-Hill Book Co. Inc.: New York.)
 GONIKBERG, M. G. (1955a).—*Adv. Chem. Moscow* **24**: 14.
 GONIKBERG, M. G. (1955b).—*C.R. Acad. Sci. U.R.S.S.* **102**: 117.
 GONIKBERG, M. G., and POVKH, G. S. (1949).—*J. Phys. Chem. Moscow* **23**: 383.
 HAMANN, S. D., and LIM, S. C. (1954).—*Aust. J. Chem.* **7**: 329.
 HAMANN, S. D., and STRAUSS, W. (1956).—*Disc. Faraday Soc.* (in press).
 MOELWYN-HUGHES, E. A., and HINSHELWOOD, C. N. (1932).—*J. Chem. Soc.* **1932**: 230.
 STEARN, E. A., and EYRING, H. (1941).—*Chem. Rev.* **29**: 504.
 WILLIAMS, E. G., PERRIN, M. W., and GIBSON, R. O. (1936).—*Proc. Roy. Soc. A* **154**: 684.

* From density measurements at 1 atm (Hamann and Lim 1954).

† From the relation $\Delta \bar{V} = -RT \frac{\partial \ln K}{\partial P}$, where K is the molal ionization constant.