Acoustical Studies VI. Observations Concerning the Behavior of Formic and Acetic Acid Vapors

C. O. Strother and W. T. Richards

impact, as suggested by Oldenberg,[12] should yield an effectiveness over deuterium which is less than two. Similarly an explanation, like that of Franck and Eucken,[13] which regards the excitation of the lower vibrational states as a prelude to chemical reaction, and consequently predicts parallel behavior for both hydrogen and deuterium, cannot be considered. Here again, since the eigenfunctions of the two molecules are practically identical, the only observable difference should be the mass factor appearing in the collision rate.

There remain two general possibilities. The first of these is concerned with the uniquely small moment of inertia of hydrogen. It appears at least possible that the magnitude of the rotational quanta which are exchanged with the ethylene molecule may be connected with the conspicuous effectiveness of hydrogen in exciting vibrational energy. If approximate "matching" or resonance occurred between a hydrocarbon vibrational quantum and a group of hydrogen rotational quanta the effect would be explained, since the distribution of rotational states of deuterium is quite different from that in hydrogen. After a preliminary survey of the computations necessary for the solution of this problem, the present writer has decided to leave

it to others. Not only is its generalized formulation exceedingly difficult, but it is believed that the present knowledge of the vibrational frequencies of ethylene is insufficient to bring it to a successful conclusion. Alternatively, it is possible that the shortness of the duration of the collision of hydrogen with ethylene, in comparison with that of deuterium under similar circumstances, may provide an explanation. According to the treatment of Zener,[14] the mass here enters exponentially. Again, however, the problem becomes difficult, since the relation between the duration of the collision and the rate of transmission of the effect of the collision appears to be the determining factor. An instantaneous blow on one of the hydrogens in ethylene would provoke severe distortional vibrations of the molecule, whereas if it were struck sufficiently slowly the result would be merely to make the molecule rotate as a whole. It must therefore be left undecided whether either of these two mechanisms is capable of providing an acceptable quantitative description of the measurements.

This investigation was originally undertaken with a view to comparing the collision efficiencies of hydrogen and deuterium found by acoustical measurements with those found from chemical reaction rates. It is somewhat ironical, therefore, that no trustworthy data for chemical reactions appear to be at present available.

[12] Oldenberg, Phys. Rev. **37**, 194 (1931); Heil, Zeits. f. Physik **14**, 31 (1932).
[13] Franck and Eucken, Zeits. f. physik. Chemie **B20**, 460 (1933).
[14] Zener, Phys. Rev. **38**, 277, 556 (1931).

Acoustical Studies

VI. Observations Concerning the Behavior of Formic and Acetic Acid Vapors

C. O. STROTHER AND W. T. RICHARDS, *Princeton University*

The thermal decomposition of formic acid at 60°, the lowest temperature at which its vapor pressure is great enough to permit the determination of the velocity of sound, was sufficiently rapid to make accurate measurements impossible. Measurements on acetic acid vapor at several temperatures are reported which serve to place the lower limit of the dissociation rate at about 10^4 sec.$^{-1}$ at 85° and 174 mm. Reasons for the variability of the velocity of sound in acetic acid, which is in sharp contrast with the behavior of nitrogen tetroxide, are discussed.

INTRODUCTION

THE success of the acoustical method in determining the dissociation rate of nitrogen tetroxide suggests its application to other rapidly dissociating gases. Among these formic and acetic acids appear especially suitable since their dissociation heats are large, and since they attain sufficient vapor pressures to permit acoustical measurements below 100°. This communication reports exploratory observations on both substances. Since the success attained was meager the report will be brief, but it is believed that the measurements were carried out with sufficient care to warrant their publication as a warning to others who may wish to undertake the same task.

APPARATUS AND PURIFICATION OF MATERIALS

The apparatus employed was essentially that already described by Richards and Reid.[1] It was, however, modified in several respects to make high temperature measurements possible. The bulb containing liquid which provided pressure regulation in the acoustical chamber (F of Fig. 3[1]) was thermostated by a vapor bath with automatic pressure control.[2] In this way the liquid was kept at constant temperature $\pm 0.01°$, and pressure regulation considerably better than that required for 0.1 percent accuracy of the velocity of sound secured in the acoustical chamber. All tubing not in the vapor bath, or in the thermostat which surrounded the acoustical chamber, was wound with calibrated chromel wire, and kept about 20° above the temperature of the acoustical chamber. The main thermostat was filled with transformer oil and controlled by a mercury regulator to $\pm 0.1°$. The necessity for preventing condensation in the tubing made the use of a quartz manometer inconvenient, and in its place a mercury manometer was employed. In this way a rough check on the vapor pressures given in the literature for formic and acetic acids was obtained. In the case of the former substance a manometer proved especially valuable since it gave an indication of the rate of decomposition. The oscillators were the same as those used for nitrogen tetroxide, but were driven by an "electron coupled" circuit which gave greater stability

and more uniform deflections at the points of maximum reaction than the oscillator previously employed.

The method of measurement was essentially that already described: the liquid was distilled into the apparatus in vacuum, frozen, and the apparatus thoroughly exhausted by a good oil pump. The acoustical chamber was then flushed many times with vapor before measurements were undertaken. Whenever possible measurements at high and at low frequency were made on the same day on the same sample of vapor. Small tube corrections, obtained as described previously, have been applied when necessary to all the values which are quoted below.

A trial with normal heptane, which was used to calibrate the apparatus, served to demonstrate that between 85° and 106° measurements reproducible to ± 0.05 percent were easily obtainable. The variability of the results recorded below is not, therefore, due to any defect in the details of measurement.

The formic acid was the commercial C. P. grade. Two samples of acetic acid were employed. Both were obtained by purification of the pure commercial acid (rated 99.5 percent). Sample I was recrystallized seven times, introduced quickly into the apparatus to prevent the accumulation of moisture, and distilled in vacuum three times. Sample II was recrystallized eight times, the melting point remaining constant after the first two crystallizations. It was then twice recrystallized in vacuum, introduced into the apparatus by the use of a "magnetic break," and three times distilled in vacuum before measurement. The melting point of both samples was 16.8°.

FORMIC ACID

Formic acid is thermodynamically unstable at ordinary temperatures, and even in glass vessels an appreciable amount of thermal decomposition of the liquid may be observed at room temperature.[3] At temperatures of 60° and above the decomposition is sufficiently rapid to require consideration even when the vapor density is being determined. Each determination of the velocity of sound requires about three hours with a gas of constant composition, and the rate of decomposi-

---

[1] Richards and Reid, J. Chem. Phys. **1**, 120 (1933), Fig. 3.
[2] Kuentzel, J. Am. Chem. Soc. **51**, 3347 (1929).

[3] Coolidge, J. Am. Chem. Soc. **50**, 2166 (1928).

tion, doubtless increased by the presence in the system of the extensive nickel and nichrome surfaces of the oscillators, proved an insuperable obstacle to accurate determinations. No measurements on formic acid are reported for this reason. The development of an acoustical method which permits rapid determinations suggests itself as the only means of overcoming this difficulty.

ACETIC ACID

The measurements on acetic acid have been summarized in Table I, which is self-explanatory. The pressures at which the measurements were made were determined from the temperature of the vapor bath and interpolation of the values for the vapor pressure of acetic acid quoted in the *International Critical Tables*. Unfortunately the measurements show variations which are larger by one order of magnitude than the experimental error. Since the variations follow, however, a relatively consistent course with time and with method of treatment, a systematic explanation suggests itself. The velocity of sound systematically increased the greater the "purity" of the sample, i.e., the larger the number of times it had been pumped out or recrystallized. Since the reverse is to be expected with a heavy vapor such as acetic acid, it appears possible that the inclusion of water in the form of a coordination compound $HAc \cdot H_2O$, similar in structure to that suggested by Sidgwick[4] for $(HAc)_2$, may here be the determining cause. The very diverse values of the density, vapor pressure, and the like encountered in the literature suggest difficulties in purification greater than those to be encountered in a mere mixture of two molecular species. If this is the case pure acetic acid, either in liquid or vapor, would be difficult indeed to obtain.

The data with which to compare these velocities are meager and sadly confused; this is perhaps the most potent reason for publishing them. The only measurement on the velocity of sound is due to Stevens[5] and cannot serve as a basis of comparison since it is at 136° and 760 mm. The most recent study of the vapor density and heat of dissociation of acetic acid is that of Fenton and Garner,[6] who found the heat of

TABLE I. *The velocity of sound in acetic acid vapor at various temperatures, frequencies, and pressures.*

Linear Frequency (kc)	Measured Velocity of Sound (m sec.$^{-1}$)	Calculated Velocity of Sound (m sec.$^{-1}$)
	Sample I	
	85.0±0.1° and 174 mm	
9.242	182.1[a]	185.8
91.26	182.3[a]	——
	95.0±0.1° and 174 mm	
9.212	190.7	193.1
91.21	190.7	——
	110.0±0.15° and 403 mm	
9.246	189.5	——
	115 ±0.15° and 403 mm	
9.218	194.0	201.9
90.80	194.3	——
	Sample II	
	84.9±0.1° and 174 mm	
9.242	183.4[b]	185.7
91.26	183.8[b]	——
	95.6±0.1° and 174 mm	
9.209	193.5	193.1
91.18	193.3	——

[a] The average of two independent determinations.
[b] The average of four independent determinations.

dissociation to be 13,790 cal. mole^{-1} at constant volume, a value somewhat higher than that reported by Ramsey and Young.[7] From the figures of Fenton and Garner and the expression of Einstein[8] for the velocity of sound in an ideal dissociating gas there result the values of 202, 193, and 186 meters sec.$^{-1}$ for the velocity of sound at low frequency and 115°, 402 mm; 95°, 174 mm; and 85°, 174 mm, respectively. These are consistently above the measured values, as Table I shows. The discrepancy cannot be attributed to neglect of the van der Waals forces, since the calculation employs the measured vapor densities, and the approximation that the gas is ideal enters only into the insensitive compressibility ratio.[9] The older data of Young[10] for the saturation densities of acetic acid are about six percent higher than those extrapolated from Fenton and Garner in the temperature range which here comes into consideration. If they are interpolated over a small pressure range by means of the ideal gas laws they give a much better agreement with experiment than is provided by the data of Fenton and Garner. This procedure is, however, not wholly defensible.

[4] Sidgwick, Chem. Soc. Ann. Reports **30**, 115 (1933).
[5] Stevens, Ann. d. Physik **7**, 320 (1907).
[6] Fenton and Garner, J. Chem. Soc., 694 (1930).

[7] Ramsey and Young, J. Chem. Soc. **49**, 790 (1886).
[8] Einstein, Sitz, Ber. Akad., 380 (1920).
[9] For a discussion of this see Richards and Reid, J. Phys. Chem. **1**, 747 (1933).
[10] Young 1910, quoted in Landholdt and Bornstein.

In view of this confusion an attempt was made to establish the vapor density and heat of dissociation by means of the acoustical measurements alone. For this purpose the velocity of sound at low frequency in a dissociating gas is written, after Einstein[8]

$$V_0{}^2 = \frac{RT(1+\alpha)}{M_2}$$
$$\times \left\{ \frac{R(B+1)^2(\alpha-\alpha^2)+2(\bar{C}_0+R)}{(RB^2+\bar{C}_0)(\alpha-\alpha^2)+2\bar{C}_0} \right\}, \quad (1)$$

where V_0 is the phase velocity of sound at low frequency, R the molecular gas constant, T the absolute temperature, α the degree of dissociation, M_2 the molecular weight of the heavy molecule, $\bar{C}_0$ the average heat capacity of double and single molecules at low frequency, and B an abbreviation for D/RT where D is the heat of dissociation at constant volume. The neglect of the van der Waals corrections in this expression is no more grave than the similar approximation usually made in obtaining the dissociation heat as, for example, in the work of Fenton and Garner.[6] Eq. (1), although cubic in α, permits the determination of $\alpha = f(P, T)$ by successive approximation because of the fact that the quantity in brackets is, with a gas of large dissociation heat and heat capacity, almost independent of temperature and very near to unity. Unfortunately the quantities for D so obtained, although centering about 14,000 cal. mole^{-1}, varied from 16,000 to 10,000 depending upon which pair of determinations was chosen for the calculation. The situation must therefore be abandoned as hopeless.

A few words should be said concerning the heat capacities employed in the calculations described above. Since there are, of course, no experimental determinations of these quantities, they must be deduced. By summing the energies of Planck-Einstein oscillators, with frequencies obtained largely from Raman spectra, values for the heat capacities of the single and double molecules were obtained which, it is believed, were not seriously in error from the standpoint of the present study. The model for the single molecule gave 12.0, 11.5, and 11.3 cal. mole^{-1} at 115, 95 and 85°; that for the double molecule 16.5, 15.7, and 15.4 cal. mole^{-1} at the same temperatures. These were used consistently in calculations concerning the low frequency velocity.

It remains only to set a lower limit for the rate of dissociation of $(HAc)_2$. Here the conditions are, of course, far less favorable than those obtaining in nitrogen tetroxide owing to the relatively large heat capacity of acetic acid. A change from the low frequency velocity, where the dissociation reaction is in equilibrium with the acoustical cycle, to the high frequency velocity where the dissociation reaction wholly fails to participate in the compressibility ratio, would mean a change of only some two to three meters sec.$^{-1}$ in the velocity of sound under the conditions here reported. As a consequence it is extremely difficult, in acetic acid, to identify the cause for any dispersion which may be found; if a part of the heat capacity fails to follow the acoustical cycle it may cause a change in the compressibility ratio comparable to a failure of the dissociation reaction. This is in sharp contrast to the conditions in nitrogen tetroxide. It is, in fact, a serious limitation of the acoustical method of determining reaction rates that it can effectively be employed only with gases of relatively low heat capacity and high dissociation heat. However, since at 85° and 174 mm no dispersion has become clearly manifest at 91 kcal., it is reasonable to attribute a minimum reaction rate of 10^4 sec.$^{-1}$ to the dissociation of $(HAc)_2$ under these conditions. It is hoped that this figure, at least, may prove of interest.