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**A Criterion for the Mechanism of the Reactions of Alkyl Halides with Hydroxylic Solvents. Reactions of Benzhydryl Chloride**

BY LESLIE C. BATEMAN, EDWARD D. HUGHES AND CHRISTOPHER K. INGOLD

The two types of mechanism which we have postulated<sup>1</sup> for aliphatic substitutions, one involving bimolecular replacement in a single stage and the other preliminary ionic fission, have been discussed recently.<sup>2</sup> The point of interest is the ionization mechanism, which we term unimolecular and Hammett polymolecular; and although in the sequel we use our own label, we strongly agree with the purpose of Hammett's, which is to emphasize the role of the solvent. We ourselves have done this in discussions,<sup>1c,3</sup> pointing out, for instance, that only through solvation is the activation energy of an ionic fission reduced to accessible values.

In a number of well-established unimolecular substitutions the entrant group comes, not from the solvent, but from a reagent present in small and controllable concentration.<sup>4</sup> For these the observed reaction order determines the mechanism. In other substitutions, for instance, the hydrolysis and alcoholysis of alkyl halides in hydroxylic solvents, the reaction order is no longer diagnostic, and other, less direct, methods must be employed. Several have been suggested,<sup>4</sup> but we need here to refer only to one particular method.

This has been illustrated with respect to the simultaneous hydrolysis and alcoholysis of *t*-butyl chloride in aqueous alcohol. The total first order reaction was first investigated by Hughes,<sup>5</sup> who found that the rate was unaffected by hydroxonium and hydroxide ions, but was much increased with increasing water content of the solvent. He concluded that the reaction was unimolecular. Olson and Halford<sup>2b</sup> examined the applicability of an equation, in constructing which they assumed the reaction to be bimo-

lecular. The formula is

$$\text{Rate} = (k_a p_a + k_w p_w) p_{\text{RCI}}$$

where the *k*'s are rate constants, the *p*'s partial vapor pressures, and the subscripts refer to alcohol, water and *t*-butyl chloride; and it may be used either to calculate the total rate, or, from the partial rates  $k_a p_a p_{\text{RCI}}$  and  $k_w p_w p_{\text{RCI}}$ , to deduce the composition of the product (ROEt + ROH). Having computed  $k_a$  and  $k_w$  from observed total rates, the authors showed that their formula gave an accurate description of the variation of total rate with solvent composition, and concluded on this account that the reaction was indeed bimolecular. Then we pointed out<sup>3</sup> that the success with which the formula represents the total rate owes nothing to the assumed mechanism, the essential postulate, the participation of solvent in the transition state, being true for all reactions in solution, including the unimolecular process. We also noted, however, that the product compositions should be calculable with a corresponding success only if the reaction is bimolecular, for in that case the product is formed in the rate-measured reaction, so that its composition is fixed by measured rate constants, whereas in unimolecular substitution the product arises subsequently to the rate-measured stage, so that its composition cannot in principle be deduced from measured constants. An application of this criterion to the reactions of *t*-butyl chloride showed that they were not bimolecular as had been claimed, and we concluded that they were unimolecular in agreement with Hughes.

The main object of this note is to point to the analogy of a second reaction of an alkyl halide with a solvent, in which a similar criterion has been applied, with results pointing again to the unimolecular interpretation. This is the reaction of benzhydryl chloride with aqueous ethanol. Like the reaction of *t*-butyl chloride, its first order rate is unaffected by hydroxonium and hydroxide ions, but is much increased with increasing water content of the solvent. Total rates have been measured by Ward, by Norris and Morton, by Kny-Jones and Ward,<sup>6</sup> and by Farinacci and

(1) (a) Hughes, Ingold and Patel, *J. Chem. Soc.*, 526 (1933); (b) Gleave, Hughes and Ingold, *ibid.*, 236 (1935); (c) Hughes and Ingold, *ibid.*, 244 (1935); (d) Hughes, Ingold and Shapiro, *ibid.*, 225 (1936).

(2) (a) Farinacci and Hammett, *THIS JOURNAL*, **59**, 2544 (1937); (b) Olson and Halford, *ibid.*, **59**, 2644 (1937).

(3) Bateman, Hughes and Ingold, *J. Chem. Soc.*, 881 (1938).

(4) References are given in paper (3).

(5) Hughes, *J. Chem. Soc.*, 255 (1935).

(6) (a) Ward, *ibid.*, 2285 (1927); (b) Norris and Morton, *THIS JOURNAL*, **50**, 1795 (1928); (c) Kny-Jones and Ward, *ibid.*, **57**, 2394 (1935).

Hammett,<sup>2a</sup> and product compositions by the last-named authors. This was before Olson and Halford's vapor pressure theory had become available, but Farinacci and Hammett noted that a bimolecular mechanism, interpreted with the aid of a concentration mass law, could not bring rates and product compositions into harmony, for when added water increased the reaction rate it did so chiefly, not by diverting the formation of benzhydryl ethyl ether into that of benzhydrol, but by accelerating the production of benzhydryl ethyl ether. Such a "catalytic" effect is, however, expected on the basis of the unimolecular mechanism.

Olson and Halford show, with respect to the example studied by them, that, whereas the vapor pressure formula exactly accounts for the variation of rate with solvent composition, a corresponding concentration formula fails completely. We have therefore considered the question of whether Farinacci and Hammett's inference is likely to be changed if this calculation is carried from the concentration basis of the assumed equation

$$\text{Rate} = (k_a'c_a + k_w'c_w)c_{\text{RCl}}$$

to the vapor pressure basis of Olson and Halford's theory. We conclude that it could not be changed. The transformation cannot, as a matter of fact, be effected completely, because the partial vapor pressures of benzhydryl chloride are unknown and would be difficult to determine accurately. We can, however, convert to the new basis the treatment of the solvent components, and, assuming an approximate invariance in the Henry's law constants of benzhydryl chloride over the relevant range of solvent compositions, test for the effect of the incompleteness of our procedure by reference to the observed total rates. For this range, the representation of the total rates is in fact so good that we have the same empirical justification as Olson and Halford for proceeding to predict the separate parts of the total rate, or, what is equivalent, the product compositions; and this is the prediction that really distinguishes the bimolecular and unimolecular mechanisms. In view of the relatively low water concentrations used, we are not surprised to find that the predicted values differ relatively little from Farinacci and Hammett's, and that therefore, as the table indicates, they show correspondingly pronounced divergences from the experimental values. Bearing in mind also the more completely investigated case of *t*-

butyl chloride, it cannot be doubted that Farinacci and Hammett's conclusions stand, *i. e.*, that the vapor pressure theory could not bring the hydrolysis and alcoholysis of benzhydryl chloride into harmony with the bimolecular mechanism.

REACTION OF BENZHYDRYL CHLORIDE WITH AQUEOUS ETHANOL AT 25°

| H <sub>2</sub> O<br>Moles/l. | $k(10^{-4}\text{min.}^{-1})$ |        | Moles % ROH          |                       |
|------------------------------|------------------------------|--------|----------------------|-----------------------|
|                              | Found                        | Calcd. | Found<br>(F. and H.) | Calcd.<br>(F. and H.) |
| 0.000                        | 343                          | ..     | ..                   | 0.0                   |
| .600                         | 474                          | 482    | 1.8                  | 31.5                  |
| 1.320                        | 634                          | 652    | 11.8                 | 51.5                  |
| 1.579                        | 691                          | ..     | ..                   | 55.1                  |

We take the opportunity to refer to four points raised by Hammett<sup>2a,7</sup> with reference to the detailed interpretation of the unimolecular mechanism, as the relevant experimental material is, and will be, considerably scattered. The first, relating to the incompleteness of racemization, is dealt with in papers<sup>8</sup> which were unavailable when he wrote. The second was that dissolved negative ions had not been found to participate in homogeneous solvolytic reactions. But they do participate if their concentration is adequate in relation to that of the reactive constituent of the solvent; thus chloroacetate ions form *t*-butyl chloroacetate without increasing the reaction rate in the hydrolysis of *t*-butyl chloride in moist formic acid, and chloride ions retard the hydrolysis of benzhydryl chlorides in moist acetone. The third point was that solvolytic reactions apparently require high concentrations of hydroxylic solvents, water having failed to react with  $\alpha$ -phenylethyl chloride in moist acetone though it accelerated the total reaction in moist acetic acid. However, we regard the difference as one of degree, depending on the ionizing properties of the solvent as a whole, and can show that hydrolyses which are slow in moist acetone are rapid in equally moist sulfur dioxide, though sulfur dioxide, like acetone, is non-hydroxylic. Fourthly, the example of sulfur dioxide illustrates how poor an index to ionizing power is the dielectric constant, doubtless because of its very indirect connection with the short-range forces determining solvation. These, however, are points of detail: as to essentials we endorse Hammett's statement<sup>7</sup> that his views and ours are in harmony.

**Summary.**—Of the bimolecular and unimolecular mechanisms of aliphatic substitution,

(7) Steigman and Hammett, *ibid.*, **59**, 2536 (1937).

(8) Hughes, Ingold and others, *J. Chem. Soc.*, 1196 *et seq.* (1937).

the former alone yields the product in a reaction stage whose rate can be measured; and therefore a comparison of rates and product compositions in competing reactions, such as those of an alkyl halide in aqueous alcohol, affords a criterion of mechanism. Such a criterion was applied by Farinacci and Hammett to the reactions of benzhydryl chloride but Olson and Halford have made proposals to change the quantitative basis of such comparisons. We consider whether Farinacci and Hammett's rejection of the bimolecular mechanism stands in the light of this work, which we have more fully examined with respect to the reactions of *t*-butyl chloride; and we conclude that it does stand. Thus the hydrolyses of *t*-butyl chloride and benzhydryl chloride are mutually confirmatory examples in which the application of the criterion mentioned favors the unimolecular mechanism, some details concerning which are discussed.

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### A New Method for the Preparation of 3,5-Cholestadiene

BY KENZO HATTORI

The various methods for the preparation of the so-called cholesterolene have been discussed recently by H. E. Stavely and W. Bergmann.<sup>1</sup> These authors also prepared 3,5-cholestadiene (I) by the Wolf-Kishner reduction of the semicarbazone of the 7-ketocholesterolene (II). Since this procedure involves prolonged heating at 180–200°, the possibility of a rearrangement of the double bonds is not excluded. In order to eliminate such possibility, 3,5-cholestadiene was prepared by the treatment of pseudocholesterolene dibromide (III) with silver nitrate in pyridine solution at room temperature.<sup>2</sup> The diene obtained by this reaction seems to be identical with the 3,5-cholestadiene described by Stavely and Bergmann.

Nine-tenths of a gram of pseudocholesterolene dibromide was dissolved in 20 cc. of pyridine containing 18% of silver nitrate. The reaction mixture was kept in the dark at room temperature for one month. The solution was then diluted with water, acidified with sulfuric acid and extracted with ether. The residue obtained on

(1) W. Bergmann, *J. Org. Chem.*, **1**, 567 (1937).

(2) E. Dane, *Z. physiol. Chem.*, **245**, 80 (1937); **248**, I (1937).

evaporation of the ether extract was recrystallized from a mixture of alcohol and ether. The diene crystallizes in needles, m. p. 79–80°,  $[\alpha]^{15D} - 68.7^\circ$ .

*Anal.* Calcd. for  $C_{27}H_{44}$ : C, 87.96; H, 12.04%. Found: C, 88.3; H, 11.7%.

The diene gave a positive reaction with Rosenheim's reagent and with antimony trichloride. Mixed with a sample of cholesterolene, prepared from cholesterol,<sup>3</sup> m. p. 79°,  $[\alpha]^{15D} - 76.0^\circ$ , it gave no depression of the melting point.

(3) Mauthner, *Monatsh.*, **17**, 34 (1896).

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### Identification of Methylisopropylcarbinol in Sharples Diethylcarbinol

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In connection with another research,<sup>1</sup> an attempt was made to obtain pure 3-pentanol by a series of careful fractional distillations of a sample of commercial diethylcarbinol supplied by the Sharples Solvents Corporation. It was noted that even after many fractionations the material of almost constant refractive index boiled over a range of 4°. Since the refractive index of methylisopropylcarbinol is very near that of 3-pentanol ( $n^{20D}$  1.4095 and 1.4100, respectively), the lower boiling portion of the sample was carefully re-fractionated by parts in an efficient column. In this way a fraction was obtained, b. p. 111.5° (732 mm.),  $n^{20D}$  1.4096, which gave the  $\alpha$ -naphthylurethan of methylisopropylcarbinol,<sup>2</sup> m. p. and mixed m. p. 108–110°.

The identification of this alcohol, which had not been found in the hydrolysis products of the chloropentanes by previous investigators,<sup>3</sup> is of considerable theoretical interest. It demonstrates that the hydrolysis of 3-chloro-2-methylbutane to the alcohol does not involve complete rearrangement. The conversion of the alcohol to the chloride even under the mildest conditions gives the rearranged product, 2-chloro-2-methylbutane.<sup>4</sup> Both these conversions are being studied further to determine the relative amounts of rearranged and non-rearranged products from each.

STATE COLLEGE, PENNA. RECEIVED SEPTEMBER 28, 1938

(1) Whitmore and Karnatz, *THIS JOURNAL*, **60**, 2536 (1938).

(2) Whitmore and Johnston, *ibid.*, **55**, 5022 (1933).

(3) Ayres, *Ind. Eng. Chem.*, **21**, 899 (1929); Clark, *ibid.*, **22**, 439 (1930).

(4) Whitmore and Johnston, *THIS JOURNAL*, **60**, 2265 (1938).