[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

# Kinetics of the Reaction of *p*-Methoxybenzhydryl Chloride with Methanol in Dilute Nitrobenzene Solution

BY PAUL D. BARTLETT AND RICHARD WILSON NEBEL

Much of the kinetic work on the reaction of organic halides with hydroxyl compounds has been done with the hydroxyl compounds as solvents.[1] These conditions obscure the manner in which the hydroxyl compound participates in the rate-determining step, which has been the subject of much debate. The present work is an effort to obtain unambiguous evidence on this point by carrying out the alcoholysis of a suitable halogen compound in an inert solvent, in which the alcohol concentration can be kept low and varied, and in which the reaction can be freed from competing reactions and made irreversible. The first of these conditions has been met in a series of experiments described by W. Taylor[2] since the inception of our work.

The dielectric constant has been considered by some to be an important factor in the effect of changing medium on the rate of solvolysis of secondary and tertiary halides.[3] With this in mind we chose an inert solvent with approximately the same dielectric constant as the alcohol taking part in the reaction. Nitrobenzene ($E = 36.1$)[4] and methanol ($E = 33.7$)[5] were selected. Nitrobenzene has the further advantage of being thoroughly inert to the kind of substances expected to be present. It was necessary, however, to establish the limits within which methanol acts as a normal, unassociated solute in nitrobenzene. This was done by a series of vapor pressure measurements, by the dynamic method, of methanol–nitrobenzene solutions at 25°. Absorption of the alcohol vapor in sulfuric acid and weighing was found precise enough to give this information. The plot of partial pressure of methanol against its formal concentration, shown in Fig. 1, indicates constancy of the size of the dissolved unit up to 0.6 molar, which means that methanol is unassociated under these conditions.

Since in dilute alcohol solutions alcoholysis of a chloride is incomplete at equilibrium, it was desirable to make the reaction irreversible if this could be done without disturbing its course. The trials for the selection of a suitable chloride were therefore made in the presence of excess piperidine, which was converted into its hydrochloride as the reaction progressed and could be titrated as a means of following the reaction. After various trials, *p*-methoxybenzhydryl chloride was selected as a halide which reacted at a convenient rate with these low concentrations of methanol. It was found, however, that there was an appreciable rate of reaction with piperidine in the absence of any methanol, and piperidine accordingly was replaced by triethylamine, which was shown to be free from this difficulty. Only after standing for a matter of months was there appreciable reaction at room temperature between the chloride and triethylamine in nitrobenzene. This great preference on the part of a secondary chloride for reacting with the weakly basic methanol rather than the more strongly basic triethylamine or even piperidine emphasizes the difference in mechanism of reaction between secondary and primary chlorides to which Ingold and Hughes have repeatedly directed attention.

In view of recent results and discussions of sol-

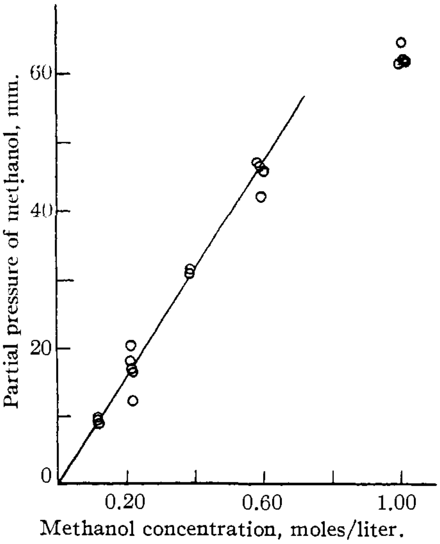

Fig. 1.

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[1] Hughes, *J. Chem. Soc.*, 255 (1935); Olson and Halford, THIS JOURNAL, **59**, 2644 (1937).

[2] Read and Taylor, *J. Chem. Soc.*, 479 (1939); Taylor, *ibid.*, 1853 (1937); THIS JOURNAL, **60**, 2094 (1938).

[3] Scatchard, *J. Chem. Phys.*, **7**, 657 (1939); Hughes, ref. 1, but see Farinacci and Hammett, THIS JOURNAL, **59**, 2542 (1937).

[4] Walden, *Z. physik. Chem.*, **54**, 129 (1906).

[5] Tereschin, *Ann. phys.*, **36**, 792 (1889).

volysis it seemed possible that, even though the chloride did not react directly with triethylamine, the reaction in the presence of both triethylamine and methanol might lead to a substantial fraction of the quaternary ammonium salt. To test this, the following experiment was performed. A solution was prepared of 0.953 g. of *p*-methoxybenzhydryl chloride with two equivalents of methanol and 1.25 equivalents of triethylamine in 50 cc. of nitrobenzene, and this solution was allowed to stand overnight. The precipitate (triethylamine hydrochloride) was filtered off and the solution was extracted three times with 10% hydrochloric acid. Then 10 cc. of the solution was concentrated under 2 mm. pressure to about 0.5 cc. and the last of the solvent removed by steam distillation. The oily residue crystallized on seeding and standing at 0°, yielding 0.195 g. of crystals melting at 19–20°, identified as impure *p*-methoxybenzhydryl methyl ether by mixed melting point with a pure sample, m. p. 27–28°. The theoretical yield was 0.189 g. of the ether. If any quaternary ammonium salt had been formed it would have passed into the water extract and the quantity of ether isolated would have been correspondingly diminished. We conclude that in titrating the amine we are following the rate of reaction between *p*-methoxybenzhydryl chloride and methanol, no reaction being involved between the chloride and the amine.

Runs carried out in the presence of only the chloride, the alcohol and the amine did not at first show good second order kinetics. The liberation of hydrogen chloride was at first excessively rapid, and the bimolecular plots did not become linear until the run was well under way. It was noted that the point of straightening of the curve in each case coincided approximately with the time at which triethylamine hydrochloride began precipitating from the solution. Apparently the building up of salt concentration was attended by a slowing of the specific reaction rate. This was confirmed by saturating the solvent in advance with triethylamine hydrochloride, which resulted in the second order plots being linear over the entire measurable reaction (in some cases more than 90%). The runs reported in this paper were all made in solutions saturated with triethylamine hydrochloride.

The solubility of triethylamine hydrochloride in nitrobenzene is markedly dependent upon the methanol concentration, even when this is small. Table I shows the solubility under the conditions of the kinetic runs.

TABLE I

SOLUBILITY OF TRIETHYLAMINE HYDROCHLORIDE IN NITROBENZENE CONTAINING METHANOL AND TRIETHYLAMINE AT 25.0°

| Concentrations in moles per liter | | |
|---|---|---|
| Methanol | Triethylamine | Triethylamine hydrochloride |
| 0 | 0 | 0.0157 |
| 0 | 0.101 | .0147 |
| 0.0833 | .102 | .0236 |
| .167 | .102 | .0356 |
| .250 | .102 | .0468 |

The slight effect of 0.1 molar triethylamine upon the solubility of triethylamine hydrochloride suggests that the large effect in the case of methanol is due to its chemical union with one of the ions of the salt, presumably with the chloride ion, to give a new and more soluble molecular species. The solubility in the solutions containing triethylamine is well expressed by

$$0.0145 + 0.1086[CH_3OH] + 0.0854[CH_3OH]^2$$

This is consistent with the idea of practically constant solubility for the molecular species $C_6H_{15}N\cdot HCl$ and the appearance of soluble $C_6H_{15}N\cdot HCl\cdot CH_3OH$ and $C_6H_{15}N\cdot HCl\cdot(CH_3OH)_2$ in amounts governed by the methanol concentration. From the solubility data we can estimate equilibrium constants

$$K_1 = \frac{[S][CH_3OH]}{[S\cdot CH_3OH]} = 0.119, \text{ and}$$

$$K_2 = \frac{[S\cdot CH_3OH][CH_3OH]}{[S(CH_3OH)_2]} = 1.27$$

where S represents triethylamine hydrochloride. This would mean that at all concentrations of methanol in nitrobenzene saturated with triethylamine hydrochloride, about 11% of the methanol is bound to the salt in a mono-alcoholate, while in the most concentrated solution about a further 4% of the methanol is bound in a di-alcoholate. This fits with the other observations made in this work and offers a satisfactory interpretation of the effect of low concentrations of methanol on the solubility of the salt.

Despite the apparent bimolecular nature of the reaction in individual runs, the bimolecular velocity constant varied markedly as the concentration of methanol was altered. A change of the methanol concentration from 0.0737 to 0.2129 caused a change in the bimolecular rate constant from 0.153 to 0.233. From the experimental results of Farinacci and Hammett[6] and the calcula-

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[6] Farinacci and Hammett, *loc. cit.*

tions of Winstein,[7] it seemed possible that there might be, superposed upon the bimolecular reaction, a trimolecular reaction involving the attack of two molecules of alcohol upon one of the chloride. The trimolecular reaction, if simultaneous with the bimolecular one, would gain in importance at higher alcohol concentrations. An equation for such superposed reactions has been derived and found to fit the present results.

If the chloride is present at a concentration $x$ and the alcohol at a concentration $(x + c)$, and the chloride is disappearing irreversibly by a bimolecular and a trimolecular path, then

$$-\mathrm{d}x/\mathrm{d}t = k_2x(x + c) + k_3x(x + c)^2$$

If the ratio $k_2/k_3$ be denoted by $r$, the integrated equation is

$$k_2t = \frac{1}{c}\ln\frac{x + c}{x} - \frac{1}{(c + r)}\ln\frac{x + c + r}{x} + \text{constant} \qquad (1)$$

Two tests of this equation are possible. A value of $r$ should exist such that the same values of $k_2$ and $k_3$ are obtained from all the runs, and the plots of Equation (1) should be linear in all cases. By successive approximations we arrived at the value $r = 0.221$, which meets these conditions. Table II summarizes the results of applying this equation to our kinetic data.

TABLE II

BIMOLECULAR AND TRIMOLECULAR VELOCITY CONSTANTS FOR THE REACTION OF *p*-METHOXYBENZHYDRYL CHLORIDE WITH METHANOL IN NITROBENZENE AT 25°, ASSUMING $k_2/k_3 = 0.221$

| Initial concentrations of | | | | | |
|---|---|---|---|---|---|
| Chloride | Methanol | Triethylamine | $k_2$ | $k_3$ | % reaction covered |
| 0.0712 | 0.0737 | 0.0908 | 0.131 | 0.593 | 82 |
| .0758 | .0780 | .0934 | .131 | .593 | 84 |
| .0723 | .1435 | .0881 | .136 | .615 | 86 |
| .0820 | .1450 | .0926 | .136 | .615 | 85 |
| .0408 | .1477 | .0901 | .131 | .593 | 94 |
| .0738 | .1549 | .1736 | ( .102) | ( .461) | 76 |
| .0705 | .1622 | .2352 | ( .091) | ( .411) | 79 |
| .0797 | .1950 | .0869 | .134 | .606 | 68 |
| .0780 | .2129 | .0851 | .127 | .575 | 77 |
| | | Average | .133 | .599 | |

The values of the rate constants, in parentheses, for the runs containing 0.1736 and 0.2352 *M* triethylamine, are not included in the average, since these large increases in the amine concentration appreciably diminish the rate of the alcoholysis. This fact and the slightly reduced solubility of triethylamine hydrochloride in the presence of tenth molar triethylamine in nitrobenzene (for which no "common ion effect" can be responsible) both suggest a slight association between methanol and triethylamine to give some such species as

$$(C_2H_5)_3N\ldots HOCH_3$$

in which the hydroxylic hydrogen is not available for hydrogen bonding and hence unable to promote either the solution of the hydrochloride or the rate of the alcoholysis.

From the average values of $k_2$ and $k_3$, we conclude that with 0.1 *M* methanol the reaction is proceeding 69% by the bimolecular and 31% by the trimolecular path. In this same case when the reaction is 75% complete, these percentages become 90 and 10, respectively. It is not surprising that the simple bimolecular formulation seems to fit these runs, since in the later stages of the reaction, when the distinction between orders of reaction is easiest to draw, the deviation from bimolecular kinetics is slight.

For reasons which have been reviewed recently,[8] we favor the interpretation of the solvolysis of secondary and tertiary halides given by Farinacci and Hammett[6] in that the rate-determining step is the removal of halogen by the alcohol or water as a solvated anion. Our present results are in harmony with this mechanism. If the solvation of a halide ion is regarded as a chemical process, there is a series of possible solvated ions involving one, two, three, etc., molecules of alcohol. The alcohol can be attached by a hydrogen bridge through any or all of the electron pairs of the halogen ion, and polymeric clusters of alcohol molecules can take the place of single alcohol molecules. By our solubility and kinetic measurements on dilute solutions we seem to have detected the ions with one and two molecules of alcohol of solvation. There is reason to suppose that at somewhat higher concentrations, where association of the alcohol becomes important, the formation of more highly solvated ions will introduce terms of higher order into the rate equation. The "polymolecular" reaction of Farinacci and Hammett would then be the predominant one in the pure alcohols and in alcohol–water mixtures.

## Experimental

*p*-Methoxybenzhydryl chloride was prepared according to Norris and Blake.[9] After purification by distillation it solidified and was recrystallized from benzene–hexane solution. It melted at 62–63°.

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[7] Winstein, THIS JOURNAL, **61**, 1635 (1939).

[8] Bartlett and Knox, *ibid.*, **61**, 3187, 3188 (1939).

[9] Norris and Blake, *ibid.*, **50**, 1811 (1928).

**Nitrobenzene,** m. p. 5.7°, was freshly distilled from phosphorus pentoxide immediately before each run. It was very light yellow in color.

**Triethylamine,** b. p. 89°, was kept over magnesium sulfate and distilled before each run from zinc and sodium.

The **methanol** used was an analytical grade giving no precipitate with aluminum ethoxide.

**Triethylamine hydrochloride** was prepared by passing hydrogen chloride gas into an ethereal solution of triethylamine. The product was recrystallized from alcohol, washed with ether, and dried for several days in a vacuum desiccator over calcium chloride.

**Vapor Pressure Measurements.**—Solutions of methanol in nitrobenzene were prepared by breaking weighed ampoules of methanol into weighed amounts of nitrobenzene. The solutions so prepared were placed in absorption towers filled with glass beads. The amount of solution used was such that in removing enough methanol for a vapor pressure determination the concentration of the methanol was not altered by more than 2%. Dried air was drawn through the absorption towers immersed in a thermostat at 25°, and then through a U-tube filled with glass beads wet with sulfuric acid. Pure nitrobenzene gave a gain in weight of the absorption tube of 0.0011 g. per 100 cc. of air passed, and a proportional blank correction was applied to each run to determine the methanol absorbed. Seventeen runs were made, at molar concentrations of methanol from 1.015 down to 0.117. Table III summarizes the results.

While these results are not very precise, the plot in Fig. 1 shows clearly the linear relationship between concentration and partial pressure of methanol up to 0.6 molar.

**The solubility determinations** were made by stirring the solutions of methanol and triethylamine in nitrobenzene with finely powdered triethylamine hydrochloride for several hours in the thermostat, extracting measured portions of the solution with water and titrating with standard silver nitrate. The solid phase present at saturation was identified as the original triethylamine hydrochloride, without any solvent of crystallization.

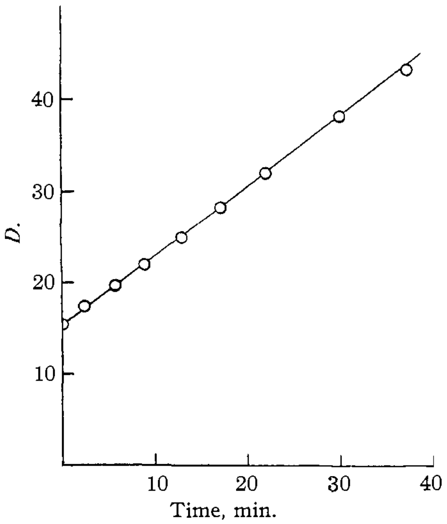

Fig. 2.

TABLE III

| Methanol concentration | Air (S. T. P.), cc. | Methanol (cor.), g. | V. p. of methanol (mm. Hg) |
|---|---|---|---|
| 1.015 | 86.8 | 0.0117 | 62.1 |
| 1.007 | 99.4 | .0135 | 62.3 |
| 1.003 | 90.8 | .0127 | 64.8 |
| 0.996 | 83.4 | .0111 | 61.6 |
| .601 | 96.8 | .0094 | 46.0 |
| .596 | 105.1 | .0093 | 42.3 |
| .589 | 131.4 | .0129 | 46.7 |
| .581 | 114.0 | .0113 | 47.2 |
| .389 | 168.6 | .0107 | 31.4 |
| .386 | 140.3 | .0090 | 31.0 |
| .217 | 153.2 | .0052 | 16.6 |
| .216 | 140.3 | .0035 | 12.3 |
| .215 | 143.6 | .0050 | 17.1 |
| .213 | 154.8 | .0065 | 20.5 |
| .211 | 150.7 | .0055 | 18.1 |
| .121 | 309.5 | .0056 | 9.0 |
| .119 | 328.0 | .0065 | 9.8 |
| .117 | 308.2 | .0059 | 9.4 |

**Technique of Velocity Determinations.**—The titrations of triethylamine were satisfactorily carried out in acetone as a titration medium using a standard solution of hydrogen chloride in ether and brom phenol blue as indicator. A solution of triethylamine was freshly prepared by adding about 0.77 cc. of it to 60 cc. of nitrobenzene and mixing. Then 55 cc. of this solution was delivered into a 125-cc. glass-stoppered Erlenmeyer flask and a weighed ampoule of methanol was broken into it. Excess solid triethylamine hydrochloride was added and the solution was shaken for several hours at 25° to attain saturation with the salt. A 5-cc. sample was then pipetted out and titrated in 50 cc. of acetone with 0.025 *N* hydrogen chloride–ether solution. The reaction was started by the addition of a weighed quantity (about 0.9 g.) of *p*-methoxybenzhydryl chloride to the 50 cc. of solution which had been brought to temperature in the thermostat. The solid dissolved rapidly, and the stop watch was started at the time of complete solution. Samples of 5 cc. were withdrawn at successive times with a pipet and titrated. The end-points were sharp and showed no tendency to drift. One 5-cc. sample was sealed in a tube and heated at 100° for several hours to get the titer corresponding to complete reaction. This provided a check on the purity of the chloride, which

TABLE IV

RUN G-14

0.3787 g. of methanol and 0.9154 g. of *p*-methoxybenzhydryl chloride in 50 cc. of nitrobenzene containing excess triethylamine and saturated with triethylamine hydrochloride. Samples of 4.99 cc. titrated with 0.02740 *N* ether–HCl solution.

| Minutes | Titer | $x$ | $x + c$ | $D$ | Per cent. reaction |
|---|---|---|---|---|---|
| 0 | 15.50 | 0.0780 | 0.2129 | 0.1541 | 0 |
| 2.42 | 13.57 | .0674 | .2023 | .1749 | 12 |
| 5.75 | 11.94 | .0584 | .1934 | .1973 | 25 |
| 8.83 | 10.60 | .0511 | .1860 | .2195 | 34 |
| 12.83 | 9.15 | .0431 | .1780 | .2494 | 45 |
| 17.00 | 7.90 | .0363 | .1712 | .2821 | 53 |
| 21.92 | 6.78 | .0301 | .1650 | .3187 | 61 |
| 29.92 | 5.31 | .0224 | .1574 | .3809 | 71 |
| 37.17 | 4.55 | .0179 | .1529 | .4312 | 77 |

proved to be better than 95%, and also on the consistency of the other measurements.

We present in Table IV the data for a typical run. The quantity $D$ in the table is

$$\log_{10}\frac{x+c}{x} - \frac{c}{c+r}\log_{10}\frac{x+c+r}{x}$$

which, according to the kinetic equation used, is expected to be proportional to time. Figure 2 shows the plot of this quantity against time.

## Summary

The rate of the reaction between methanol and *p*-methoxybenzhydryl chloride in dilute nitrobenzene solution under irreversible conditions has been studied as a function of the methanol concentration from 0.07 to 0.21 *M*. There is a bimolecular reaction involving one molecule of the chloride and one of methanol and at the same time a trimolecular reaction involving one molecule of chloride and two of methanol. It is suggested that mechanisms of higher order appear as the alcohol is made more concentrated, as seems probable also from the work of Farinacci and Hammett.

Vapor pressure measurements have been made, showing that methanol is not associated in nitrobenzene solutions of the strength used.

The solubility of triethylamine hydrochloride in nitrobenzene is altered markedly by small concentrations of methanol. A series of solubility measurements are interpreted as giving evidence of specific solvation of the chloride ion by one and by two molecules of methanol.

Triethylamine is inert toward *p*-methoxybenzhydryl chloride in nitrobenzene solution, at least in comparison to like concentrations of methanol. This makes it possible to use triethylamine to combine with hydrogen chloride liberated in the alcoholytic reaction and thus to make the reaction effectively irreversible.

CAMBRIDGE, MASSACHSETTS RECEIVED MARCH 27, 1940

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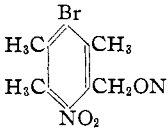
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

# Polymethylbenzenes. XXVI. The Nitration of Bromopentamethylbenzene

BY LEE IRVIN SMITH AND JAMES W. HORNER, JR.[2]

When bromodurene is nitrated under certain circumstances, the product is 6-nitro-3-bromo-2,4,5-trimethylbenzyl nitrate, I.[3] Similarly, 5-bromopseudocumene or its 3,6-dinitro derivative can be attacked at the side chain by nitric acid,[4] and the product has been shown to consist of an inseparable mixture of two benzyl nitrates, II and III.[5]



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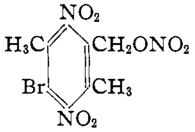
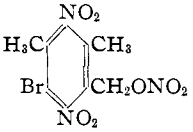


II



III

These nitrates usually can be converted into aromatic nitro compounds by action of sulfuric acid. Peculiar orientation effects frequently are observed when polyalkylbenzenes are converted into substitution products by reactions in which an alkyl group is simultaneously removed or replaced.[6] The most striking of these effects is perhaps that shown by the nitration of pentamethylbenzene[7] and of pentaethylbenzene[8] to dinitrotetraalkylbenzenes in yields of over 70%, and with an ortho orientation of the nitro groups in the methyl derivative and a para orientation in the ethyl derivative. The easy decomposition of benzyl nitrates to nitro compounds indicates that these substances may well be intermediates in those reactions in which alkyl groups are replaced by nitro groups and that the peculiar orientation effects observed in such reactions are due to factors which determine which one of several alkyl groups will be attacked.

In order to study further these effects, the nitration of bromopentamethylbenzene (IV) has been examined. When fuming nitric acid was added to a solution of IV in chloroform, there resulted an oily solid from which was isolated a mixture of two isomeric bromotetramethylbenzyl nitrates, V

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(1) XXV, THIS JOURNAL, **62**, 771 (1940).

(2) Abstracted from a thesis by James W. Horner, Jr., submitted to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the Ph.D. degree, January, 1940.

(3) (a) Smith and Tenenbaum, THIS JOURNAL, **57**, 1293 (1935); (b) Smith, Taylor and Webster, *ibid.*, **59**, 1082 (1937).

(4) Huender, *Rec. trav. chim.*, **34**, 25 (1915).

(5) Rinkes, *ibid.*, **57**, 1405 (1938); *ibid.*, **58**, 218, 538 (1939).

(6) (a) Baur, *Ber.*, **27**, 1614 (1894); (b) Barbier, *Helv. Chim. Acta*, **11**, 152, 157 (1928); (c) de Cappeller, *ibid.*, **11**, 426 (1928); (d) Battegay and Kappeler, *Bull. soc. chim.*, **35**, 989 (1924).

(7) Smith and Harris, THIS JOURNAL, **57**, 1289 (1935).

(8) Smith and Guss, unpublished work.