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Kinetic Behavior of the Long-lived *p*-Anisylcamphenilyl Cation in Formic Acid Solutions

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Kinetic evidence, together with preparative evidence previously reported,[1] leads to an interpretation of the behavior of the long-lived *p*-anisylcamphenilyl cation (II) in formic acid solutions which is shown in Chart 1. The rate constants k_a, k_b, k_c and k_d are all too rapid to measure. When I or IV is dissolved in 96.8% formic acid, the fraction F of the material existing as the carbonium ion (λ_{max} 384 mμ, ϵ 51,000) is the sum of two exponentials as in eq. 1. Application of an integrated form of eq. 1 allows evaluation of the following rate constants in sec.$^{-1}$ at 25°: $k_1 = 4.78 \times 10^{-3}$, $k_2k_c/k_d = 1.21 \times 10^{-3}$, $k_3 = 0.53 \times 10^{-3}$, $k_4k_c/k_d = 0.69 \times 10^{-3}$. k_1 is believed to represent the rate constant for a Nametkin rearrangement within the carbonium ion. In 100% formic acid the optical density of a solution of *p*-anisylapocamphene (IV) reaches a maximum within 2 minutes. The rate constants have been approximately evaluated and it appears that the only important difference from 96.8% formic acid is the increase of 0.86 unit in the negative value of the acidity function H_0, which correspondingly increases the value k_c/k_d. Solutions of *p*-anisylapocyclene (VII), epi-*p*-anisylcamphenilol (VIII), the formates isolated from reaction of *p*-anisylcamphenilol (I) in formic acid for four minutes and four hours, and alcohols obtained from such formates all follow eq. 1. *p*-Anisylapocyclene (VII) is equilibrated with the carbonium ion much more slowly than *p*-anisylapocamphene (IV) but is favored at equilibrium relative to IV. The rate constant for racemization of (−)-*p*-anisylapocamphene in formic acid, 6×10^{-4}, is close to that predicted from Chart 1 using values of k_5 and k_6 estimated from the spectrophotometric kinetic measurements on *p*-anisylapocyclene (VII), the only symmetrical compound in the series.

Introduction

In a previous paper[1] it was shown that both *endo*- and *exo*-2-*p*-anisylcamphenilols (Ia and Ib) dissolve in formic acid with immediate formation of a long-lived carbonium ion (II) having an absorption maximum at 384 mμ, ϵ 51,000. In 96.8% formic acid this ion rapidly approaches equilibrium with the olefin, 2-*exo*-methyl-2-*endo*-*p*-anisyl-3-methylenenorbornane ("*p*-anisylapocamphene," IV). The resulting equilibrium mixture is then more slowly converted into a mixture of formates, possible representatives illustrated by the formulas V and VI, which has different compositions when made from I and from IV. Optically active I gives rise to optically active IV, showing that the absorbing ion has no plane of symmetry. These facts, together with the production of formates of opposite signs (and differing magnitudes) of rotation from I directly or *via* IV, led us to assign structure II to the stable carbonium ion and to deduce the existence of an isomeric ion III derived from it by a Nametkin rearrangement, and in turn rapidly equilibrated with the olefin IV.

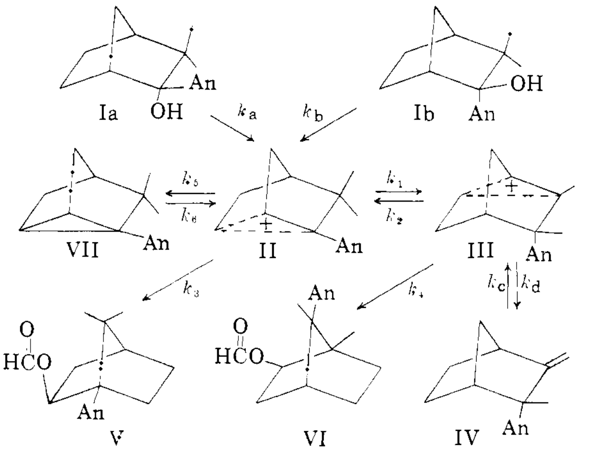

CHART 1

An = $CH_3OC_6H_4$-*p*

The kinetic curves from spectrophotometric or conductimetric observation of these changes in 96.8% formic acid have an important characteristic in common (Fig. 1). If the logarithm of optical density or of conductivity is plotted against time, there is a steep descent, a bend, and finally a linear portion extending to the end of the reaction. Although the conductimetric curve in Fig. 1 represents a thousandfold higher concentration than the spectrophotometric curve, the qualitative and quantitative similarities of these curves leave no doubt that the light-absorbing species in the one experiment is identical with the conducting species in the other.

Kinetics of the Reaction in 96.8% Formic Acid.—Enough molecular species have been identified in these transformations so that, if all the rate constants were of comparable magnitude, the kinetics would be hopelessly complex. Certain simplifying relationships could, if present, reduce the kinetics to the case of two successive or concurrent reversible reactions of first order, the general solution to which[2] is of the form

$$F = ae^{-\lambda_2 t} + be^{-\lambda_3 t} + F_\infty \qquad (1)$$

where F is any quantity (such as optical density) proportional to the concentration of one of the participants in the reacting series, and F_∞, its value at infinite time, may be zero. Whenever this treatment is applicable, if $\lambda_2 > \lambda_3$, the first term will eventually become negligible relative to the second, and a plot of ln F *vs.* time will approach linearity, with slope λ_3. This straight line, extrapolated to zero time (intercept = b), permits the evaluation of the second term of eq. 1 corresponding to each experimental point earlier in the run. The first term of eq. 1 can now be evaluated by difference and the linearity of its log plot verified as a test of the adequacy of eq. 1.

In Fig. 2 it is shown that the optical density at 384 mμ of a solution of *p*-anisylcamphenilol in 96.8% formic acid is a function of time having this form. The ordinates in this plot are percentages of the initial optical density, plotted on a logarithmic

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[1] P. D. Bartlett, E. R. Webster, C. E. Dills and H. G. Richey, Jr., *Liebigs Annalen*, **623**, 217 (1959).

[2] See A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 160–164; T. M. Lowry and W. T. John, *J. Chem. Soc.*, **97**, 2634 (1910); F. A. Matsen and J. L. Franklin, THIS JOURNAL, **72**, 3337 (1950). Although there is no λ_1, the notation of eq. 1 is chosen for correspondence to that of Matsen and Franklin, Frost and Pearson.

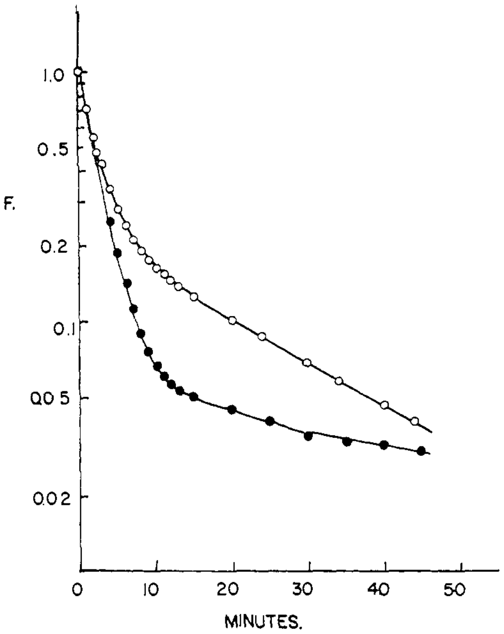

Fig. 1.—Comparison of spectrophotometric and conductimetric observation of the carbonium ion from *p*-anisylcamphenilol (I) in 96.8% formic acid: open circles, $F = D/D_0$, optical density at 384 mμ expressed as a fraction of the extrapolated optical density at zero time; solid circles, $F = (\Lambda - \Lambda_\infty)/(\Lambda_0 - \Lambda_\infty)$, electrical conductivity in excess of that at infinite time, expressed as a fraction of the extrapolated initial value of this quantity. In both solutions the *p*-anisylcamphenilol was added as a dioxane solution. For the upper curve, $[\mathrm{I}]_0 = 4.66 \times 10^{-5}$ *M*, dioxane ~1%; for the lower curve, $[\mathrm{I}]_0 = 0.045$ *M*, dioxane ~8.7%. The differing dioxane contents are considered responsible for the quantitative differences between the curves.

scale. The straight line of steeper slope represents the first term of eq. 1, calculated as described above. This resolution into two straight lines shows that the optical density does not depend upon more than two successive reactions of differing but measurable rate. The sequence IV → V involves *three* consecutive reactions; it can fit eq. 1 only if one of the three processes occurs immeasurably fast relative to the others. We shall now describe the evidence which indicates which of these reactions is the fast one.

The interconversions of three molecular species in first-order reactions are indicated mathematically in the scheme[2]

$$\begin{tikzcd}
A_1 \arrow[rr, shift left, "k_{12}"] \arrow[dr, shift left, "k_{13}"] & & A_2 \arrow[ll, shift left, "k_{21}"] \arrow[dl, shift left, "k_{23}"] \\
& A_3 \arrow[ul, shift left, "k_{31}"] \arrow[ur, shift left, "k_{32}"] &
\end{tikzcd}$$

CHART 2

The solution to the differential equations is always in the form of eq. 1, with or without F_∞ having an appreciable value; however, with various *k*'s or combinations of *k*'s equal to zero, the coefficients and exponents in eq. 1 become different functions of the remaining *k*'s, and the physical interpretation of the slopes and intercepts thus depends upon which *k*'s are assumed to vanish. We may begin by defining the absorbing species as A_2. A first simplification comes from the observation that the final optical density of the solutions in 96.8% formic acid is almost negligible, so that $k_{31} \cong 0 \cong k_{32}$. With A_3 formed irreversibly, it makes no difference whether A_3 is a single chemical species, as represented in the formal equations of Chart 2, or whether a different product is formed from A_1 and from A_2, as represented in the chemical equations, where II forms V and III forms VI. In all our experiments k_a is immeasurably great, so the harmonizing of the chemical reactions in Chart 1 with the four-constant scheme of Chart 2 minus k_{32} and k_{31} requires only a decision as to whether the pair (II, III) or the pair (III, IV) are in rapid equilibrium.

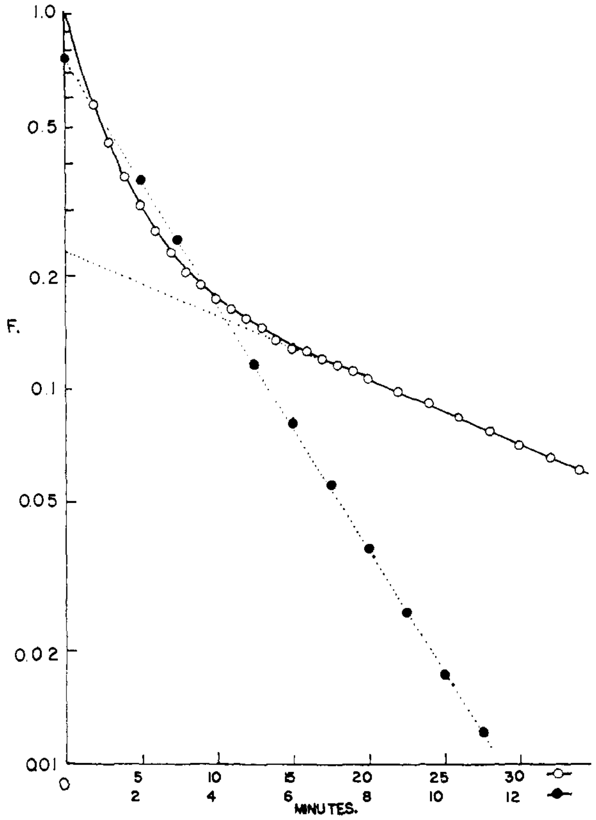

Fig. 2.—Example of the determination of λ_2, λ_3 and *b* from an experimental curve of *F* (log scale) *vs.* time for *p*-anisylcamphenilol (open circles, upper time scale). The slope of its final linear portion, in units of (ln *F*) (sec.$^{-1}$), is $-\lambda_3$; its intercept, shown by the dotted projection, in units of *F*, is *b*. The solid circles (lower time scale) represent the first term of eq. 1, determined by subtracting from the ordinate of each open circle before $t = 12$ min. the ordinate of the corresponding point on the dotted line. The slope of the line defined by the solid circles (in units of (ln *F*) (sec.$^{-1}$)) is $-\lambda_2$; its intercept is *a;* solvent: 96.8% formic acid.

It is clear from the preparative experiments[1] that II and III cannot be in rapid equilibrium. The mixture of formates isolated from the reaction of IV in formic acid is structurally different from that isolated with I as a starting material, and has a

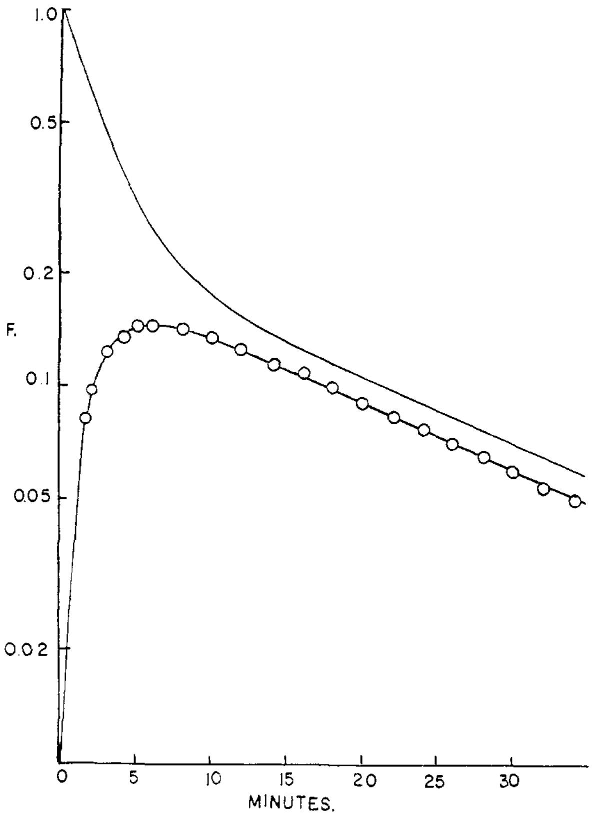

Fig. 3.—Rise and decline of optical absorption at 384 mμ due to carbonium ion formed from *p*-anisylapocamphene (IV) in 96.8% formic acid. Upper curve shows behavior of *p*-anisylcamphenilol (I) under similar conditions, confirming that IV is the colorless substance involved in the initial rapid decline of absorption in the ion from I. In each case *F* is optical density, expressed as a fraction of its value for total formation of carbonium ion.

different sign of optical rotation. Moreover, as appears from Fig. 3, final product is formed as fast from solutions of IV in formic acid which are still acquiring color as from solutions of II with maximum absorption, produced by dissolving I. Therefore the ion III, structurally related to IV and formed from it, can yield final product at a rate comparable or superior to that at which it is equilibrated with the ion II. At the same time we should expect this ion to be comparable in stability to the short-lived camphenyl-isobornyl ion rather than to the rapidly formed and long-lived ion II. We continue to attribute the optical absorption to II, and consider that the high reactivity of III prevents its accumulation in appreciable amounts compared with II.

If k_1 and k_2 are to be measurable rate constants, then k_c and k_d must be immeasurably great, or eq. 1 would not express the kinetics of the system. By analogy it is quite reasonable that III and IV should be in mobile equilibrium in formic acid as a solvent. In a number of solvents the equilibrium between camphene and the camphenyl-isobornyl cation is established more rapidly than the Wagner–Meerwein or Nametkin rearrangement occurs.[3,4] We shall then proceed to apply the kinetic equations with the following identifications between the chemical equations of Chart 1 and the formal scheme of Chart 2.

$A_1 = (\text{III} \rightleftarrows \text{IV}) \cong \text{IV}$
$A_2 = \text{II}$
$A_3 =$ final products, whether V or VI
$k_{12} = k_2k_c/k_d$
$k_{21} = k_1$
$k_{13} = k_4k_c/k_d$
$k_{23} = k_3$
$k_{31}, k_{32} = 0$
k_a, k_b, k_c, k_d very great
k_5, k_6 very small

Under these conditions with $F = (A_2)/(A_2)_0$, the coefficients of eq. 1 have the values[5]

$$a = \frac{\lambda_2 - k_{12} - k_{13}}{\lambda_2 - \lambda_3} \qquad (2)$$

$$b = \frac{k_{12} + k_{13} - \lambda_3}{\lambda_2 - \lambda_3} \qquad (3)$$

The process of integration provides two further equations

$$\lambda_2\lambda_3 = k_{12}k_{23} + k_{13}k_{21} + k_{13}k_{23} \qquad (4)$$

$$\lambda_2 + \lambda_3 = k_{12} + k_{13} + k_{21} + k_{23} \qquad (5)$$

These four equations do not suffice for the determination of the four unknown rate constants, since eq. 2 and 3 are interdependent and afford only the same information, namely, the value of $(k_{12} + k_{13})$. The complete solution is made possible by kinetic runs starting with the olefin IV (Fig. 3), in which $(A_2) = (A_3) = 0$ at $t = 0$; the optical density rises from zero to reach a maximum at about the time when the curve from I reaches its maximum curvature. The latter parts of the initially ascending curve from IV and the descending curve from I are identical in slope and nearly so in position. A knowledge of the molecular extinction coefficient (51,000)[1] of the ion II by extrapolation of the descending curve from I makes it possible to plot the ascending curve from IV using $(\text{II})/(\text{IV})_0 = (A_2)/(A_1)_0$ as ordinate; then

$$a' = -b' = \frac{-k_{12}}{\lambda_2 - \lambda_3} \qquad (6)$$

The inclusion of eq. 6 makes it possible to evaluate all four of the rate constants. They have the values at 25° shown in Table I. Each λ for 96.8% acid is an average of three runs from alcohol and one run from olefin; *b* was 0.212 and *b′* was 0.205 in this solvent.

TABLE I

RATE CONSTANTS FOR REACTIONS OF THE 2-*p*-ANISYLCAMPHENILYL CATION IN FORMIC ACID SOLUTION AT 25°

Constant according to Chart 2	Constant according to Chart 1	Value of constant $(\text{sec.})^{-1} \times 10^3$ in 96.8% formic acid	Value of constant $(\text{sec.})^{-1} \times 10^3$ in 100% formic acid (approx.)
k_{12}	k_2k_c/k_b	1.21	17
k_{21}	k_1	4.78	4
k_{13}	k_4k_c/k_b	0.69	8
k_{23}	k_3	0.53	0.6
λ_2		6.57	27
λ_3		0.66	1.6

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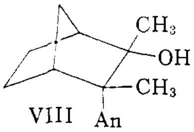
[3] H. Meerwein and K. van Emster, *Ber.*, **55B**, 2500 (1922).

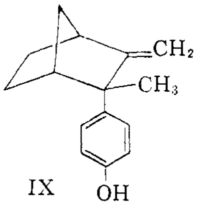
[4] P. D. Bartlett and I. Pöckel, THIS JOURNAL, **60**, 1585 (1938).

[5] We are indebted to Mr. Charles L. Perrin for the integration of the rate equations for this special case, which differs from those in ref. 2. The same set of equations has been integrated and applied recently by E. S. Lewis and M. D. Johnson (THIS JOURNAL, **82**, 5399 (1960)) to a problem involving a diazonium ion, diazohydroxide and diazotate.

Kinetics in Anhydrous Formic Acid.—The kinetic course of the reaction of 2-*p*-anisylcamphenilol (I), *p*-anisylapocamphene (IV), *p*-anisylapocyclene (VII), *epi-p*-anisylcamphenilol (VIII), 2-*p*-hydroxyphenylcamphenilol (IX), formates isolated after four minutes and four hours, and the alcohols recovered from such formates have all been followed spectrophotometrically in anhydrous formic acid at 25°. In all cases eq. 1 is followed, with F passing through a maximum, and values of λ_2 and λ_3 can be estimated except that λ_3 in the case of the four-hour formate was not distinguishable from zero during the period of measurement. The latest measurement in any experiment was the value of $F = 0.027$ at 420 minutes for *p*-anisylapocamphene (IV). This time is 57 half-lives for the late curve from IV, but only 2.4 half-lives for that from the cyclene (VII). Therefore only the data for IV were corrected for F_∞ before plotting. In view of the succession of reactions with decreasing rates, such corrections can only be approximate. Table II shows the values of λ_2, λ_3 and b' and the time of maximum optical density (t_{max}) for these cases; see also Fig. 4.



VIII



IX

In anhydrous formic acid the curve of log $(A_2)/(A_2)_0$ against time starting with 2-*p*-anisylcamphenilol (I) deviates only slightly from a straight line. The ascending curve from the olefin IV is near its maximum by the time of the first point, causing considerable uncertainty in the measurement of λ_2. Moreover, the values of the rate constants from application of eq. 2 to 6 in 100% formic acid are highly sensitive to the purity of the olefin IV. The sample of IV used in the kinetic runs took up 99% of the calculated hydrogen over platinum oxide, but this olefin was difficult to prepare entirely free from *p*-anisylapocyclene (VII), and no peaks observed in the infrared curve of the latter were ever totally absent from preparations of the olefin. Also the acidity of formic acid is very sensitive to small amounts of water. In view of these difficulties the values of the constants in 100% formic acid cannot be considered as certain as those in the part aqueous medium. Table I includes a listing of these approximate values, and it can be seen that k_{12} and k_{13} are greater in anhydrous than in 96.8% formic acid by an order of magnitude, while k_{21} and k_{23} have nearly the same values in the two solvents. This is consistent with the known change in H_0 from -0.90 in 96.8% formic acid to -1.76 in anhydrous formic acid.[6] According to the correspondence of constants previously indicated, k_{12} and k_{13} both contain the ratio k_c/k_d, which is the ratio of concentrations of a positively charged acid to its neutral base. This quantity should, accordingly, be over seven times as great in anhydrous as in 96.8% formic acid.

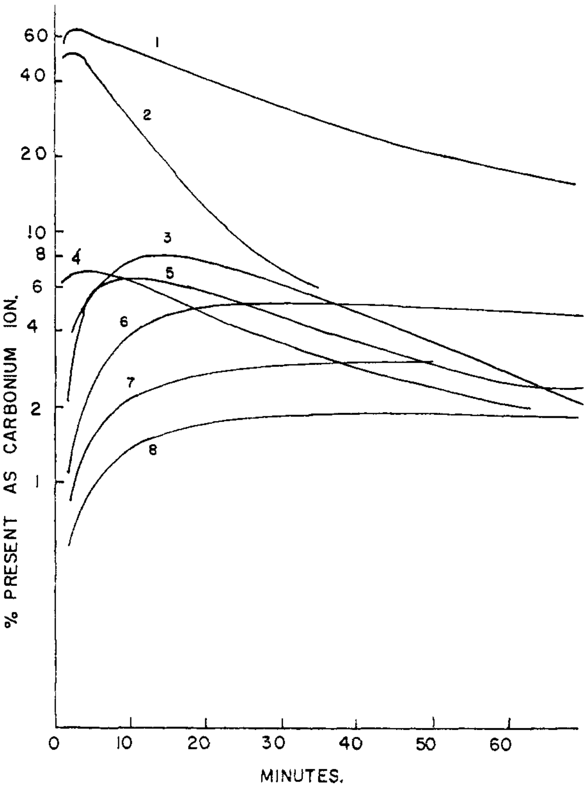


Fig. 4.—Spectrophotometric observation of compounds yielding the *p*-anisylcamphenilyl cation (or, in the case of curve 1, the *p*-hydroxyphenylcamphenilyl cation) in 100% formic acid: 1, *p*-hydroxyphenylapocamphene (IX) (ordinates assigned assuming same ϵ_{334} for its ion as for the *p*-anisylcamphenilyl cation); 2, *p*-anisylapocamphene (IV); 3, epi-*p*-anisylcamphenilol (VIII); 4, alcohol mixture from formate isolated after 9 minutes; 5, alcohol mixture from formate isolated after 4 hours; 6, *p*-anisylapocyclene (VII); 7, formate isolated after 4 hours; 8, formate isolated after 4 minutes.

The constant k_1 of Chart 1 or k_{21} of Chart 2 is of special interest, as it represents the direct measurement of the rate of a Nametkin rearrangement within a carbonium ion, the conversion happening in this case to be from the more stable to the less stable isomeric ion.

The assignment of individual rate constants to the reacting systems starting with *p*-anisylapocyclene or with the various alcohols and formates presents some complexities and will not be carried further here. It is known from previous experiments[1] that *p*-anisylapocylene is readily formed from *p*-anisylcamphenilol in ether half-saturated with hydrogen chloride and also on shaking a chloroform or petroleum ether solution of *p*-anisylcamphenilol for four minutes with 98^+% formic acid. The yield of *p*-anisylapocyclene reaches 32% of the dehydration product under these conditions but becomes very small if the solution of *p*-anisylcamphenilol in formic acid is allowed to stand for several hours. The behavior of *p*-anisylapocyclene in the kinetic experiment in formic acid is consistent with this; t_{max} is 35 minutes compared to 2 minutes for

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(6) L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 4239 (1932). The value in 96.8% formic acid was estimated from their equations.

p-anisylapocamphene (IV) and b' is only a tenth of the value it has starting from the olefin. These facts indicate that the three-membered ring is slowly attacked by acid in contrast to the olefin, but at equilibrium the cyclene may even be favored relative to the olefin. In time both give way to formates, which are formed still more slowly but with more favorable equilibria.

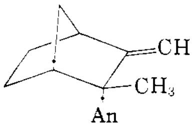
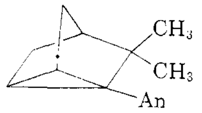
With any of a number of kinetic assumptions it is possible to translate the quantities in Table II into sets of rate constants, but our data do not provide enough internal checks to make this seem a worthwhile procedure. One such manipulation, however, is of considerable interest. *p*-Anisylapocyclene (VII) is the only compound in Chart 1 or Table II which has a plane of symmetry. Starting with optically active *p*-anisylapocamphene (IV), racemization should be observed if our conclusion is correct that this material soon passes into equilibrium with the cyclene. With the assumption that in Chart 2, as applied to VII as starting material, $k_{13} = 0$, a simplified determination of three rate constants is possible suggesting that the rate constant for conversion of the ion II into the cyclene VII is of the order of 6×10^{-4} sec.$^{-1}$. Using the values of k_{12} and k_{21} for anhydrous formic acid in Table I, we conclude that the rate constant for conversion of an equilibrated solution of IV with II into VII should be 5×10^{-4}. A sample of *p*-anisylapocamphene having a specific rotation $[\alpha]_D$ −47.7° was dissolved in 98$^+$% formic acid and the total hydrocarbon fraction recovered after twenty minutes at which time its specific rotation had declined to −22.9°. These figures correspond to a rate constant for racemization of 6×10^{-4} sec.$^{-1}$ in 98$^+$% formic acid at room temperature, which is in surprisingly close agreement with that estimated from the separate rate constants. This check should be valid whether or not the olefin was mixed with cyclene when recovered.

In the preparative experiments[1] a good yield of the olefin IV from solution of the alcohol in 98$^+$% formic acid was favored by the concentrations chosen. The alcohol I dissolved completely as ion, but the hydrocarbon separated so that it was removed from the formic acid solution as formed. In the experiments using a non-polar extractant the proportion of cyclene VII formed in a few minutes was markedly greater than in its absence. This has been attributed previously[7] to an effect of the dissolved portion of the extractant on the ionizing power of formic acid. It may also have been due in part or entirely to the experimental circumstance that in the presence of the extractant shaking was continued throughout the experiment, thus preserving active equilibration between phases and causing the olefin to restore the concentration of ion II, which in the formic acid was continuously yielding cyclene.

Neither the tertiary alcohol epi-*p*-anisylcamphenilol (VIII) nor any tertiary formate was ever found among the reaction products in formic acid solution. We suppose, therefore, that the observed conversion of VIII into carbonium ion in 100% formic acid is irreversible and that k_{21} for this system should be assumed equal to zero if we were going to calculate rate constants from this kinetic experiment. It may be a little surprising that this tertiary alcohol has a smaller λ_2 than either of the secondary alcohol mixtures in Table II. This may be due to the fact that the two secondary alcohols arise from formates produced directly from the carbonium ion II and hence presumably have the hydroxyl group located in the *exo* position where its ionic removal is greatly facilitated by electronic delocalization simultaneous with the ionization process. On the other hand, epi-*p*-anisylcamphenilol (VIII) is the reaction product of methyllithium on *p*-anisylapocamphenilone[8] and probably has the methyl group in the less hindered *exo* position. Anchimeric assistance to the ionic removal of the hydroxyl group is, therefore, lacking, and the rate is slow although the product ion III does not return to the epi-alcohol or its formate.

Table II

Behavior of Compounds Related to 2-*p*-Anisylcamphenilol in 100% Formic Acid at 25°

Compound	$10^3 \lambda_2$, sec.$^{-1}$	$10^3 \lambda_3$, sec.$^{-1}$	b'	t_{max}, min.
	27	1.6	0.65	2
IX	~26	0.47	(~0.70)[a]	3
	1.8	.066	.062	35
VIII	2.5	.48	.35	14
"9-Minute alcohol"	6.9	.50	.085	5
"4-Hour alcohol"	4.5	.39	.089	11
"4-Minute formate"	2.0	.009	.019	40
"4-Hour formate"	2.0	. . .	.030	>45

[a] Assuming ϵ_{max} for *p*-hydroxyphenilyl cation to be the same as for *p*-anisylcamphenilyl cation. The former has its absorption maximum at 378 mμ instead of 384 mμ.

Reaction in Concentrated Hydrochloric Acid.—One experiment was carried out in which *p*-anisylcamphenilol was dissolved in concentrated hydrochloric acid. The products were not isolated, but the kinetics was observed to follow eq. 1 with $F_\infty \neq 0$. This corresponds to a final position of equilibrium with 25% of the material in the form of absorbing carbonium ion. The constants of this curve are $\lambda_2 = 5.5 \times 10^{-3}$, $\lambda_3 = 4.4 \times 10^{-4}$, $F_\infty = 0.25$ and $b = 0.44$. Here the quantity plotted to obtain the resolution of the curves is $\log (F - F_\infty)$. This case would appear to be parallel to the classically investigated equilibria of camphene hydrochloride and the bornyl chlorides. If our previous surmise is correct that the isolated chloride from *p*-anisylcamphenilol and hydrogen chloride in ether has the structure of 1-anisylapoisobornyl chloride (X), then there remains its *endo* epimer and the two epimeric chlorides structurally related to the formate VI to be brought into equilibrium with the ion. No further isolation experiments were conducted upon this system.

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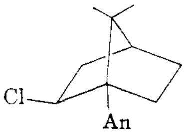
(7) Reference 1, p. 226–227.

(8) Reference 1, pp. 223, 243.



X

Experimental

Preparations.—All the compounds used in the kinetic experiments have been previously reported and their preparations described.[1]

Solvents.—Commercial dioxane was purified by the method of Hess and Frahm.[9] It was found necessary to continue the initial heating with hydrochloric acid for nearly a week. The material used boiled at 100.7-100.9°, had a constant refractive index of 1.4204 at 25° throughout the distillation, and showed no detectable absorption at 384 mμ.

Anhydrous formic acid was prepared in various ways. Distillation of reagent grade 88% formic acid (Merck and Company) with phthalic anhydride after a 6-hour reflux period gave about 75% yield of apparently anhydrous material. A drying of 88% formic acid with freshly prepared anhydrous copper sulfate for several days gave an acid 94% pure by titration. Distillation yielded a fraction boiling at 99.0-99.2° (uncor.) which by titration showed a purity of 100.1%. Titration of formic acid (Eastman Kodak Co.) showed a purity of 99.6% and that from the Victor Chemical Co. gave figures of 98.25 and 98.34%. Freezing points of formic acid samples were determined with thermometers calibrated by the Bureau of Standards. Some samples were also titrated: 1.5 g. of formic acid was diluted with 50 g. of water, and then 5 g. of this solution was titrated to a phenolphthalein end-point with 0.1 *N* sodium hydroxide. Eastman $98^+\%$ formic acid was used for most of the non-kinetic experiments. Samples from three bottles of this acid had freezing points of 7.57°, 7.47° and 7.87°. These corresponded to formic acid concentrations of 99.56, 99.49 and 99.75% assuming that water was the sole impurity and using 8.25° as the freezing point of formic acid and 2.77 degrees per mole per 1000 g. as the cryoscopic constant. Two independent titrations of the sample with a freezing point of 7.87° gave values of 99.59 and 99.53% formic acid. Samples of Eastman acid were distilled through vacuum-jacketed columns packed with small rings. A small amount of the distillate was discarded, and then about two-thirds of the material was collected within a range of 0.2° at about 101°. A sample distilled through a 51-cm. column had a freezing point of 8.17°, corresponding to 99.95% formic acid; two independent titrations gave values of 99.97 and 99.97% formic acid. Two other samples distilled through a 101-cm. column had freezing points of 8.19° and 8.26°, corresponding to 99.96 and 100.01% formic acid. Other concentrations of formic acid were made by dilutions by weight.

Kinetics Procedure.—The standard solutions of formic acid were made up gravimetrically. One ml. of water was pipetted into a 50-ml. volumetric flask and weighed. Formic acid was then added to the mark, and the flask was again weighed. This gave 98.4% formic acid. The other acid solutions were made up similarly. A concentrated stock solution of the reactant solute was prepared containing 10 mg. in 10 ml. of dioxane, and approximately 100 mg. of this solution was weighed into a 10-ml. volumetric flask. This flask was then filled to the mark with the desired standard acid, shaken vigorously for 30 seconds, and placed in the quartz spectrophotometer cells. The determination of the spectrum was started immediately. Runs with the isomeric 2-*p*-anisylcamphenilols, using the Cary spectrophotometer, were carried out at the temperature of a thermostated room (about 26°). All other runs were made with a Beckman DU spectrophotometer using a thermostated cell holder which has been described.[10] These runs were made at either of two thermostat settings, 25.06 ± 0.03° or 25.00 ± 0.03°.

Continuous spectra were taken with a Cary recording spectrophotometer in 100.0% formic acid from 325 to 450 mμ on all the materials related to *p*-anisylcampheniol: *p*-anisylapocyclene, *p*-anisylapocamphene, epi-*p*-anisylcamphenilol, the formates isolated after 4 minutes and after 4 hours from reactions of *p*-anisylcamphenilol and formic acid, and the alcohol mixtures obtained from the formates isolated after 9 minutes and after 4 hours from this reaction. The spectra were taken when the absorptions of the solutions were about at their maxima, and several spectra were taken in succession for those solutions whose absorptions were rapidly changing. Identical spectra were observed in all these cases.

For the determination of conductivity, a solution of *p*-anisylcamphenilol was made in dioxane. The alcohol is not too readily soluble in this solvent, and hence more dioxane was needed than might have been desirable. Three grams of the dioxane solution which had been allowed to come to temperature in a thermostat at 25.0° was added to 30.43 g. of 96.8% formic acid that had been similarly thermostated. The solution was shaken vigorously and then poured into a conductivity cell (Central Scientific Co. no. 7005) having a cell constant of 0.307. The conductivity bridge used was a Central Scientific Co. type 70000 employing an "electric eye" null indicator. During the conductivity run, the cell was thermostated at 25.0°.

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[9] K. Hess and H. Frahm, *Ber.*, **71B**, 2627 (1938).

[10] Designed by F. H. Westheimer and J. Kumamoto; see P. D. Bartlett and R. E. Davis, THIS JOURNAL, **80**, 2514 (1958).

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICH.]

A Stable Dipositive Carbonium Ion[1,2]

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Evidence is presented for the existence of dipositive carbonium ion II, produced by the ionization of trichloromethylpentamethylbenzene (I) in 100% sulfuric acid according to equation 1. The significance and generality of the results are discussed.

Carbonium ion theory has been invaluable in interpreting many organic reactions, and numerous types of carbonium ions have been discovered or suggested. Some are stable and unequivocally established through the isolation of crystalline salts; others are reaction intermediates for which the evidence is inferrential, but sometimes overwhelming.[4] With the exception of ions produced in a mass spectrometer or by other high energy means,[5]

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[2] For a preliminary account, see THIS JOURNAL, **80**, 5894 (1958).

[3] Petroleum Research Fund Fellow, 1958–1960.

[4] For an excellent brief review, see D. Bethell and V. Gold, *Quart. Revs.*, **12**, 173 (1958).

[5] See F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957, pp. 183–185.