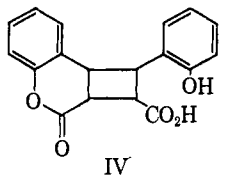
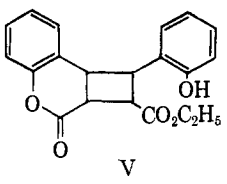
and remelted at 178.8–179.3°, the melting point of II. The infrared spectrum of the material had bands, *inter alia*, at 3410, 1755, and 1710 cm.$^{-1}$. The product is believed to be a mixture of IV and V, and is probably formed by reaction with water and ethanol during isolation.



IV



V

The combined weight of all fractions was 0.506 g. (~15%). Since a different material was isolated, the yield cannot be compared with those in the parallel experiments, but the result does show that dimerization occurs even with a coumarin:benzophenone ratio of 720.

Effect of Acetophenone.—A solution of 3.48 g. of coumarin and 0.06 g. of acetophenone in 25 ml. of benzene was irradiated in a Pyrex tube for 79.5 hr. The product was recrystallized from ethyl acetate–toluene giving 392 mg. (11%) of a material that melted at 159.6–161.9° with evolution of a vapor, resolidified, and remelted at 178.8–179.3°, the melting point of II. The product initially isolated is believed to be VI and/or V formed by ring opening by adventitious water or alcohol d ring isolation (*vide supra*).

Effect of Fluorenone.—A solution of 3.48 g. of coumarin and 0.06 g. of fluorenone in 25 ml. of benzene was irradiated in a Pyrex tube for 79.5 hr. with unfiltered light. Two products were isolated, 441 mg. (12.7%) of II and 856 mg. (24%) of the ring-opened product (*vide supra*) derived from II.

Direct Irradiation in Benzene at High Dilution.—Twenty 12 × 100 mm. Kimex tubes were loaded with 3 ml. each of 0.01 *M* solutions of coumarin in benzene. The solutions were degassed with three freeze–thaw cycles, sealed *in vacuo*, and irradiated for 71 hr. with unfiltered light from th 450-watt lamp. The contents of the tubes were combined and solvent was removed by evaporation under a stream of air. The residual scum was taken up in hot toluene and after four recrystallizations yielded 10 mg. (11%) of II, m.p. 179.8–180.6°. The infrared spectrum was identical with that of pure II.

Direct Irradiation in Benzene–Ethanol.—A 16-g. sample of coumarin was dissolved in a mixture of 100 ml. of benzene and 25 m . of ethanol and divided among four Pyrex tubes. The solutions were flushed with nitrogen, sealed, and irradiated with unfiltered light for 94 hr. The product was isolated and recrystallized from glacial acetic acid, giving 320 mg. (2 %) of I.

Direct Irradiation in Dioxane–Ethanol.—A solution of 3 g. of coumar'n in 2 ml. o ethanol and 2 ml. of dioxane was placed in a Pyrex tube, flushed with nitrogen, sealed, and irradiated for 82 hr. with unfiltered light. The yellow solution was worked up as usual, yielding 24 mg. (0.8% of I after one recrystallization.

Irradiation in Dimethyl Sulfoxide.—A solution of 3.48 g. of coumarin in 30 ml. of DMSO was irradiated in five nitrogen-flushed, Pyrex tubes with unfiltered light for 76.5 hr. The yellow solution was concentrated at 1 mm., leaving a viscous yellow residue. Benzene was added and crystals slowly formed. The infrared spectrum of the product was identical with that of an authentic sample of I; yield 130.8 mg. (3.7%).

rradiation in **Dimethylformamide.**—The experiment was a duplicate of the previous one except that the solvent was 30 ml. of DMF. The yield of I was 70.3 mg. (2%).

Irradiation in Acetic Acid.—The experiment was a duplicate of the previous two except that 3.0 g. of coumarin was dissolved in 30 ml. of glacial acetic acid and irradiation was terminated after 48 hr. The yield of I was 0.643 g. (21.4%).

Irradiation of Ethyl Coumarate.—A solution of 1.01 g. of ethyl coumarate in 30 ml. of benzene was degassed, sealed *in vacuo*, and irradiated in a Pyrex tube with unfiltere i light for 72.5 hr. Only coumarin was isolated from the mixture.

An identical experiment was carried out with 0.99 g. of benzophenone added to the mixture. A crystalline product which separated during irradiation was recrystallized three times from benzene and sublimed *in vacuo* to give 50 mg., white crystals, m.p. 198°. The product was not further investigated.

A solution containing 1.005 g. of ethyl coumarate and 0.102 g. of coumarin in 30 ml. of benzene was degassed and irradiated with unfiltered light for 72.5 hr. Only coumarin could be isolated from the mixture.[11]

Acknowledgment.—This study was partially supported by a grant from the National Science Foundation.

(11) NOTE ADDED IN PROOF.—Recent measurements suggest strongly that transfer of singlet energy from coumarin to benzophenone involves emission and reabsorption of light.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY, PITTSBURGH 13, PENNA.]

Chemical Behavior of Charge-Transfer Complexes. II. Phenanthrene Catalysis in Acetolysis of 2,4,7-Trinitro-9-fluorenyl *p*-Toluenesulfonate[1,2]

BY ALLAN K. COLTER, SAMUEL S. WANG, GEORGE H. MEGERLE, AND PAUL S. OSSIP

RECEIVED MARCH 16, 1964

Acetolysis of 2,4,7-trinitro-9-fluorenyl *p*-toluenesulfonate (I) is accelerated by added phenanthrene. Rates of acetolysis were measured at a series of phenanthrene concentrations at 55.85, 70.0, 85.0, and 99.9°. Rates increase with increasing phenanthrene concentration up to 5.16 times the uncatalyzed rate at 0.086 *M* phenanthrene (70.0°), the highest concentration studied. Apparent (formal) activation parameters (70.0°) vary from $\Delta H^{\pm}$ = 25.7 kcal. mole^{-1}, $\Delta S^{\pm}$ = −11.7 e.u. mole^{-1}, in the absence of phenanthrene, to $\Delta H^{\pm}$ = 22.4 kcal. mole^{-1}, $\Delta S^{\pm}$ = −18.3 e.u. mole^{-1} at 0.08 *M* phenanthrene. The data were analyzed in terms of a mechanism involving 1:1 complexing between phenanthrene and substrate. The analysis leads to values of K_T, the equilibrium constant for 1:1 complex formation, and k_c, the specific rate of acetolysis of the 1:1 complex, at 55.85, 70.0, and 85.0°. The 1:1 complex is 21 to 27 times as reactive in acetolysis as uncomplexed substrate at these temperatures. Values of K_T are in good agreement with values estimated by an independent spectrophotometric study. Activation parameters for acetolysis of the 1:1 complex were estimated to be $\Delta H^{\pm} \simeq 26$ kcal. mole^{-1} and $\Delta S^{\pm} \simeq -5$ e.u. mole^{-1}, showing that the 1:1 complex is more reactive in acetolysis than the uncomplexed substrate because of a more favorable entropy of activation. The significance of these results is discussed.

Introduction

The field of organic molecular complexes of the donor–acceptor type has been a very active one during the past decade.[3] However, relatively little attention appears to have been given to the possible effects of complex

(1) A preliminary report of a portion of this work has appeared: A. K. Colter and S. S. Wang, *J. Am. Chem. Soc.*, **85**, 115 (1963) (part I of this series).

(2) Abstracted in part from a thesis submitted by S. S. Wang in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology, June, 1961.

(3) G. Briegleb, "Electronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961.

formation on the chemical properties of an organic donor or acceptor. The present paper and subsequent papers in this series will describe a systematic investigation of such effects.

In the initial phases of this program we have been investigating the possibility that a reaction of an organic donor or acceptor may be subject to specific catalysis by charge-transfer complexing with a nonreacting acceptor or donor, respectively. Complex formation will produce a rate enhancement in a reaction in which complexing lowers the free energy of the transition state more than that of the ground state. A reaction in which an organic donor passes through a transition state which, for any reason, is a better donor than the initial state should be accelerated by a nonreacting acceptor. Likewise, a reaction of an organic acceptor in which the transition state is a better acceptor than the initial state should be accelerated by nonreacting donor. There are several kinds of reactions where such catalytic effects might be anticipated.

Several earlier studies having some bearing on the general question of modification of chemical properties by involvement in a charge-transfer complex have been reported. In 1928, Brønsted,[4] measuring the relative acidities of a series of organic acids in benzene solvent by means of an indicator method, found picric acid (pK_a in water at 25° $\simeq$ 0.71) to fall between monochloroacetic acid ($pK_a \simeq 2.87$) and dichloroacetic acid ($pK_a \simeq 1.30$) in acidity. This decrease in acidity of picric acid relative to the carboxylic acids is even more remarkable when it is noted that the dissociation constant of picric acid is generally *less sensitive* to changes in solvent ion solvating ability than that of a carboxylic acid.[5] In the 1930's, Brønsted, Bell, and co-workers[6] carried out several investigations designed to test the applicability of the Brønsted catalysis law in nonpolar aprotic solvents. For the isomerization of N-bromoacetanilide in chlorobenzene[6a] the catalytic constants of ten carboxylic acids and phenols were well correlated with their pK_a's in aqueous solution by means of a Brønsted catalysis law expression, while the catalytic effectiveness of picric acid was about $^1/_{15}$ that predicted by this expression. Similar results were obtained for the acid-catalyzed mutarotation of *l*-menthone[6b] and the acid-catalyzed reaction of phenol with ethyl diazoacetate in benzene.[6c] The unexpectedly low acidity of picric acid in the aromatic solvents can be accounted for by charge-transfer complexing between picric acid and the solvent; it is interesting, however, that neither Brønsted nor Bell considered complexing as a possible explanation of their results.

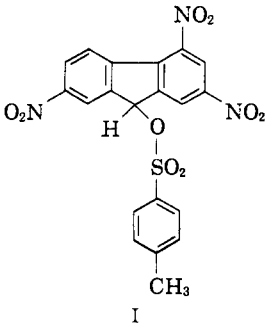
In 1954, Ross and co-workers[7a] found the reaction of picryl chloride with triethylamine in chloroform to be retarded by added hexamethylbenzene. Assuming that the 1:1 complex makes no contribution to the observed rate constant, Ross calculated a minimum value for the equilibrium constant for complex formation between picryl chloride and hexamethylbenzene. The value so obtained was more than ten times larger than that determined spectrophotometrically; however, later work[7b] showed that the discrepancy could be accounted for in terms of a solvent effect, the amount of complex formation being highly dependent on the concentration of amine. The retarding effect of hexamethylbenzene could be a result of electronic or steric influences, or both.

Leffler and Hubbard[8] have examined the effect of the acceptor 1,3,5-trinitrobenzene in several radical decomposition reactions in diethyl malonate solvent. Addition of 0.2 *M* trinitrobenzene resulted in an apparent increase of about 20% in the rate of decomposition of hexaphenylethane, but the effect was judged to be close to the experimental uncertainty. Addition of 0.15 *M* trinitrobenzene had no measurable effect on the rate of decomposition of 1,2-di(*p*-methoxyphenyl)tetraphenylethane. Similarly, the rate of decomposition of phenylazotriphenylmethane was unaffected by *ca.* 0.25 *M* trinitrobenzene.

In 1955, Smith and Leffler[9] published rate data for solvolysis of *p*-nitrobenzhydryl bromide in 90% acetone–water. They added approximately 1 *M* hexane, benzene, *m*-dimethoxybenzene, *p*-dimethoxybenzene, and nitrobenzene, all at the expense of acetone. All increased the rate, the rate enhancements ranging from 14 to 39% at 50°. However, hexane had the largest effect, next to *m*-dimethoxybenzene, and *p*-dimethoxybenzene the smallest effect, next to benzene; hence it was evident that at least one other factor besides π-complexing must be important in this case.

In 1959, Graybill and Leffler[10] reported a study of solvent effects in the racemization of the dimethyl ester of 2,2′-dimethoxy-6,6′-dicarboxybiphenyl. In chloroform solvent at 100°, 0.23 *M* 1,3,5-trinitrobenzene produced a 14% increase in rate. A much smaller rate enhancement (*ca.* 2%) was produced by 0.07 *M* 2,4,7-trinitrofluorenone in acetonitrile solvent at 100°. Unfortunately the effect of trinitrobenzene, besides being small, is in the direction expected on the basis of solvent effects *not* involving charge-transfer complexing.[10]

In the present study we sought to maximize catalytic effects due to charge-transfer complexing by appropriate choice of reaction and reactant. Acetolysis



I

of 2,4,7-trinitro-9-fluorenyl *p*-toluenesulfonate (I) seemed ideal for several reasons. First, the fluorene ring system is planar, and positive charge developed at the 9-position in the transition state should be well delocalized. Secondly, the related ketone 2,4,7-trinitrofluorenone has been shown[11] to be a very effective accep-

(4) J. N. Brønsted, *Ber.*, **61**, 2049 (1928).

(5) (a) L. A. Wooten and L. P. Hammett, *J. Am. Chem. Soc.*, **57**, 2289 (1935); (b) A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

(6) (a) R. P. Bell, *Proc. Roy. Soc.* (London), **A143**, 377 (1934); (b) R. P. Bell and E. F. Caldin, *J. Chem Soc.*, 382 (1938); (c) J. N. Brønsted and R. P. Bell, *J. Am. Chem. Soc.*, **53**, 2478 (1931).

(7) (a) S. D. Ross, M. Bassin, M. Finkelstein, and W. A Leach, *ibid.*, **76**, 69 (1954); (b) S. D. Ross, M. M. Labes, and M. Schwartz, *ibid.*, **78**, 343 (1956).

(8) J. E. Leffler and R. A. Hubbard, II, *J. Org. Chem.*, **19**, 1089 (1954).

(9) B. B. Smith and J. E. Leffler, *J. Am. Chem. Soc.*, **77**, 2509 (1955).

(10) B. M. Graybill and J. E. Leffler, *J. Phys. Chem.*, **63**, 1461 (1959).

(11) (a) M. Orchin and E. O. Woolfolk, *J. Am. Chem. Soc.*, **68**, 1727 (1946); (b) M. Orchin, L. Reggel, and E. O. Woolfolk, *ibid.*, **69**, 1225 (1947).

TABLE I

ACETOLYSIS OF 2,4,7-TRINITRO-9-FLUORENYL *p*-TOLUENESULFONATE IN THE PRESENCE OF PHENANTHRENE

55.85 ± 0.01°		70.0 ± 0.01°		85.0 ± 0.01°		99.9 ± 0.02°	
10^2[donor], M[a]	10^7k, sec.$^{-1}$	10^2[donor], M[a]	10^5k, sec.$^{-1}$	10^2[donor], M[a]	10^5k, sec.$^{-1}$	10^2[donor], M[a]	10^5k, sec.$^{-1}$
0	1.66 ± 0.03	0	0.775 ± 0.002	0	0.454 ± 0.006[b]	0	1.86 ± 0.02
0.971	2.56 ± .01	1.906	1.60 ± .04	4.67	1.12 ± .05	0.931	2.36 ± .03
1.94	3.29 ± .09	3.81	2.32 ± .04	5.62	1.27 ± .02	1.86	2.86 ± .02
3.89	4.99 ± .04	4.76	2.71 ± .06	6.57	1.41 ± .04	3.72	3.61 ± .01
4.85	5.72 ± .09	5.72	3.03 ± .04	7.50	1.52 ± .03	5.58	4.35 ± .03
5.82	6.33 ± .05	6.67	3.41 ± .04	8.44	1.62 ± .03		
6.79	7.05 ± .03	7.62	3.50 ± .03				
		8.58	4.00 ± .03				

[a] Concentrations are corrected for solvent expansion and refer to the temperature of the kinetic measurements. [b] This and other rates at 85.0° were repeated since our preliminary report (ref. 1) and differ slightly from those reported earlier.

tor. Finally, choice of acetic acid as solvent favors solvolysis of the limiting type[12,13] more than the aqueous acetone solvent used by Smith and Leffler[9] and also avoids the complications inherent in the use of mixed solvents.[9]

Added donors did indeed produce substantial rate enhancements. The general evidence for charge-transfer complexing as the source of these effects has been summarized in a preliminary report.[1] The present paper describes a study of the acetolysis of I in the presence of phenanthrene.

Results

Kinetic Studies.—First-order rate constants for acetolysis of 2,4,7-trinitro-9-fluorenyl *p*-toluenesulfonate (**I**) at four temperatures, in the absence of donor and in the presence of a series of concentrations of phenanthrene, are listed in Table I. The product of acetolysis of I in the absence of donor, carried out in refluxing glacial acetic acid, is 2,4,7-trinitro-9-fluorenyl acetate, isolated in quantitative yield.[14] The same product was also recovered, along with unreacted I and unchanged phenanthrene, as the only isolable product from the combined titrated rate samples in an acetolysis at 99.9° with 0.056 M phenanthrene.

Plots of observed rate constant *vs.* stoichiometric donor concentration are nearly linear, with gentle regular downward curvature. Using these plots, values of observed rate constants at 0.05 M phenanthrene (four temperatures) and 0.08 M phenanthrene (70.0 and 85.0°) were estimated, and these in turn used to calculate apparent activation parameters in the presence of 0.05 and 0.08 M phenanthrene (Table II).

TABLE II

APPARENT ACTIVATION PARAMETERS[a]

10^2[donor], M	$\Delta H^{\pm}$ (70.0°), kcal. mole^{-1}	$\Delta S^{\pm}$ (70.0°), e.u. mole^{-1}
0	25.7 ± 0.4	−11.7 ± 1.2
0.05	22.9 ± 0.3	−17.6 ± 0.8
0.08	22.4[b]	−18.3[b]

[a] Activation parameters are listed with their standard deviations, obtained in the usual way from a least squares analysis of the log k *vs.* $1/T$ plots. [b] Calculated from two rate constants (70.0, 85.0°); estimated uncertainties, *ca.* ±0.5 kcal. mole^{-1} and ±1.5 e.u. mole^{-1}, respectively.

Spectrophotometric Studies.—As a complementary study, 1:1 complex formation between I and phenanthrene was investigated spectrophotometrically at 35, 45, and 55°. Optical densities of 8 to 13 mixtures of I ($5.96–13.2 \times 10^{-4}$ M, 35°) and phenanthrene ($2.34–7.92 \times 10^{-2}$ M, 35°) in glacial acetic acid were measured at 390 and 400 mμ at the three temperatures. The data were treated using the Ketelaar modification[15] of the Benesi–Hildebrand equation[16] (1)

$$\frac{[A]_0}{E_\lambda - \epsilon_\lambda^{A}[A]_0} = \frac{1}{\epsilon_\lambda^{D\cdot A} - \epsilon_\lambda^{A}} + \frac{1}{K_T[D]_0(\epsilon_\lambda^{D\cdot A} - \epsilon_\lambda^{A})} \quad (1)$$

$[A]_0$ and $[D]_0$ are the stoichiometric concentrations of acceptor I and donor (phenanthrene), respectively, ϵ_λ^{A} (measured directly) and $\epsilon_\lambda^{D\cdot A}$ are the molar extinction coefficients of acceptor and 1:1 complex, E_λ is the measured optical density of the mixture, and K_T is the equilibrium constant for the reaction

$$A + D \rightleftharpoons D\cdot A$$

The validity of this equation in the present work is considered in the Experimental section.

Least squares analyses of plots of $[A]_0/(E_\lambda - \epsilon_\lambda^{A}[A]_0)$ *vs.* $1/[D]_0$ led to estimates of K_T and $\epsilon_\lambda^{D\cdot A}$ which are listed, with their standard deviations, in Table III. Average values of K_T were used to calculate the entropy and enthalpy of complex formation.

Tentative Mechanism of Phenanthrene Catalysis.—The simplest mechanism for catalysis of the acetolysis by phenanthrene and other donors[1] involves 1:1 complex formation.

$$\begin{array}{ccc} \text{ROTs} + \text{D} & \overset{K_T}{\rightleftharpoons} & \text{ROTs}\cdot\text{D} \\ \text{HOAc}\downarrow k_u & & \text{HOAc}\downarrow k_c \\ \text{ROAc} + \text{D} & \overset{K_A}{\rightleftharpoons} & \text{ROAc}\cdot\text{D} \\ + & & + \\ \text{HOTs} & & \text{HOTs} \end{array}$$

ROTS and ROAc represent I and its acetolysis product, respectively, D is donor, ROTs·D and ROAc·D are 1:1 complexes, and HOTs is *p*-toluenesulfonic acid; K_T and K_A are equilibrium constants for 1:1 complex formation; k_u and k_c are the specific rates of acetolysis of complexed and uncomplexed *p*-toluenesulfonate, respectively.

(12) S. Winstein, E. Grunwald, and H. W. Jones, *J. Am. Chem. Soc.* **73**, 2700 (1951).

(13) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(14) A. K. Colter and S. S. Wang, *J. Org. Chem.*, **27**, 1517 (1962).

(15) J. A. A. Ketelaar, C. van de Stolpe, A. G. Goudsmit, and W. Dzcubas, *Rec. trav. chim.*, **71**, 1104 (1952).

(16) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

TABLE III

SPECTROPHOTOMETRIC STUDY OF 1:1 COMPLEX FORMATION

Temp., °C.	Wave length, mμ	K_T,[a,b] l. mole^{-1}	$\epsilon\lambda^{D\cdot A}$, l. mole^{-1} cm.$^{-1}$	$\Delta H°$ (45°), kcal. mole^{-1}	$\Delta S°$ (45°), e.u. mole^{-1}
35	390	5.00 ± 1.08 } Av.[c] 4.86 ± 0.55	2099 ± 345		
	400	4.81 ± 0.64	1519 ± 171		
45	390	4.01 ± 1.08 } Av.[c] 3.96 ± 0.68	2290 ± 486	4.83 ± 0.29[d]	12.45 ± 0.92[d]
	400	3.93 ± 0.87	1629 ± 310		
55	390	2.76 ± 1.58 } Av.[c] 3.00 ± 1.00	2800 ± 1323		
	400	3.16 ± 1.29	1781 ± 633		

[a] These values differ somewhat from those reported earlier (ref. 1); they are based on the old measurements plus additional measurements. [b] Based on 13 measurements at 35°, 12 at 45°, and 8 at 55°. [c] Weighted averages (see Experimental). [d] These standard deviations reflect only scatter in the log K_T *vs.* $1/T$ plot and not uncertainties in K_T.

In terms of this mechanism, the rate is given by

$$\frac{-d\{[ROTs] + [ROTs\cdot D]\}}{dt} = \frac{-d[ROTs]_0}{dt} = \frac{d[HOTs]}{dt} = k_u[ROTs] + k_c[ROTs\cdot D] \quad (2)$$

where $[ROTs]_0$ is the stoichiometric concentration of I at time t. The observed first-order rate constant, k_{obsd}, is given by

$$k_{obsd} = \frac{-d[ROTs]_0}{dt} \div [ROTs]_0 = k_uF_u + K_cF_c = k_u + (k_c - k_u)F_c \quad (3)$$

where F_u and F_c are the fractions of the reactant which are uncomplexed and complexed, respectively, at time t. Strict first-order behavior requires F_c to be constant throughout the course of the rate, a situation which will be realized if $K_A \simeq K_T$ or if $[D]_0 >> \{[ROTs\cdot D] + [ROAc\cdot D]\}$. The second of these conditions is met in all rates reported herein; in addition, it is unlikely that K_A and K_T differ greatly.

The equilibrium condition for 1:1 complex formation involving the reactant is given by eq. 4.

$$K_T = \frac{[ROTs\cdot D]}{[ROTs][D]} = \frac{[ROTs\cdot D]}{\{[ROTs]_0 - [ROTs\cdot D]\}\{[D]_0 - [ROTs\cdot D] - [ROAc\cdot D]\}} \quad (4)$$

Under conditions where $[D]_0 >> \{[ROTs\cdot D] + [ROAc\cdot D]\}$ eq. 4 simplifies to

$$K_T = \frac{[ROTs\cdot D]}{\{[ROTs]_0 - [ROTs\cdot D]\}[D]_0} = \frac{F_c}{[D]_0(1 - F_c)} \quad (5)$$

Combination of eq. 3 and 5, with elimination of F_c, leads to

$$\frac{1}{(k_{obsd} - k_u)} = \frac{1}{(k_c - k_u)} + \frac{1}{K_T[D]_0(k_c - k_u)} \quad (6)$$

which predicts a linear relation between $1/(k_{obsd} - k_u)$ and $1/[D]_0$. Incursion of one or more pairs of ion pair intermediates (*e.g.*, R^+OTs^- and $R\cdot D^+OTs^-$) which are directly interconvertible may, under special circumstances, lead to more complex relationships between k_{obsd} and $[D]_0$; however, the present results (see below) do not appear to demand a mechanism more complex than the one proposed.

Plots of $1/(k_{obsd} - k_u)$ for the results at 55.8, 70.0, and 85.0° are shown in Fig. 1, 2, and 3. The data were

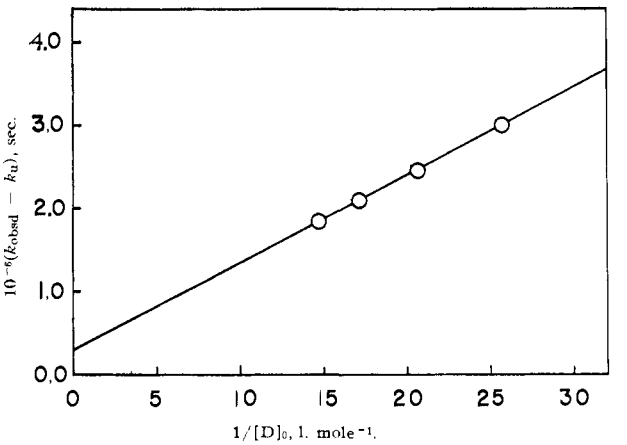


Fig. 1.—Plot of $10^{-6}/(k_{obsd} - k_u)$ *vs.* $1/[D]_0$, 55.85°.

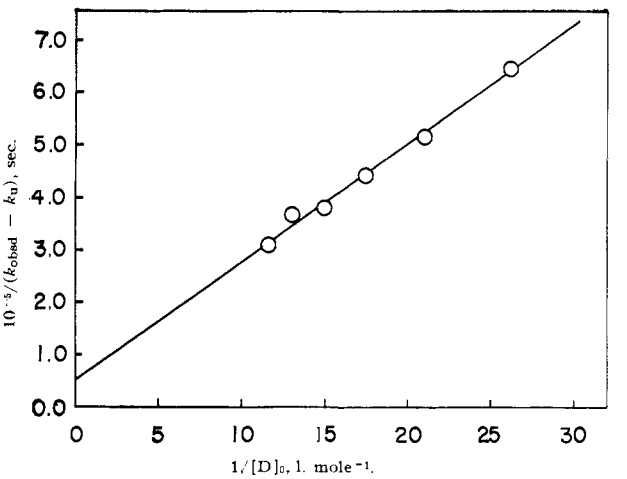


Fig. 2.—Plot of $10^{-5}/(k_{obsd} - k_u)$ *vs.* $1/[D]_0$, 70.0°.

analyzed by means of a weighted least squares procedure (Experimental). Table IV lists values of k_c and K_T so

TABLE IV

RESULTS OF ANALYSIS OF KINETIC DATA[a]

Temp., °C.	k_c, sec.$^{-1}$	k_c/k_u	K_T, l. mole^{-1}	K_T, l. mole^{-1} (extrap. from spectrophotometric results)
55.85	(3.5 ± 0.3) × 10^{-6}	21 ± 2	2.8 ± 0.3	3.0
70.0	(2.1 ± 0.5) × 10^{-5}	27 ± 6	2.2 ± .7	2.2
85.0	(9.6 ± 2.0) × 10^{-5}	21 ± 4	1.7 ± .5	1.6

[a] Uncertainties taken as standard deviations obtained from simple least squares analyses of 4 points of highest [donor] at 55.85°, 6 points of highest [donor] at 70.0°, and 4 points of highest [donor] at 85.0°. The K_T's so obtained were 3.4, 2.4, and 1.9 l. mole^{-1}, respectively.

TABLE V

ACTIVATION PARAMETERS FOR ACETOLYSIS OF THE 1:1 COMPLEX

Temp., °C.	Indirect procedure: k_cK_T/k_u,[a] l. mole^{-1}	Indirect procedure: $\Delta H^{\pm}$ (70.0°),[b] kcal. mole^{-1}	Indirect procedure: $\Delta S^{\pm}$ (70.0°),[b] e.u. mole^{-1}	Direct procedure: k_cK_T/k_u,[c] l. mole^{-1}	Direct procedure: $\Delta H^{\pm}$ (70.0°),[d] kcal. mole^{-1}	Direct procedure: $\Delta S^{\pm}$ (70.0°),[d] e.u. mole^{-1}
55.85	55[a]			59		
70.0	55	26.3 ± 1.4	−3.9 ± 4.1	59	25.9 ± 0.5	−5.0 ± 1.5
85.0	32			37		
99.9	28			. .		

[a] Initial slopes of plots of k_{obsd}/k_u *vs.* $[D]_0$; estimated uncertainties *ca.* ±5 l. mole^{-1}. [b] From least squares analysis of plot of log (initial slope) *vs.* $1/T$ (4 temperatures) and $\Delta H_u^{\pm}$, $\Delta S_u^{\pm}$, $\Delta H°$, and $\Delta S°$ from Tables II and III. [c] Directly calculated from values of k_c, K_T, and k_u in Tables I and IV. [d] From least squares analysis of plot of log k_c (Table IV) *vs.* $1/T$; uncertainties are standard deviations from least squares analysis.

obtained, values of k_c/k_u at the three temperatures, and K_T's extrapolated from the spectrophotometric results assuming $\Delta H°$ for complex formation to be approximately constant over this range of temperatures (see Discussion). The two sets of K_T's agree well within the limits of experimental uncertainty. Insufficient data are presently available at 99.9° to make any reasonable estimate of K_T at this temperature.

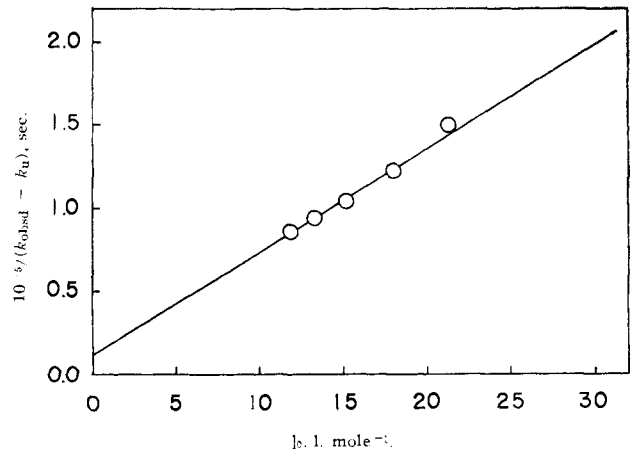


Fig. 3.—Plot of $10^{-5}/(k_{obsd} - k_u)$ *vs.* $1/[D]_0$, 85.0°.

Activation Parameters for Acetolysis of the 1:1 Complex.—Assuming the proposed mechanism to be essentially correct, it is of interest to know how the transition state for acetolysis of the 1:1 complex differs from that for the uncomplexed *p*-toluenesulfonate. Some information on this question can be gained by comparison of the activation parameters for the two processes. The activation parameters for acetolysis of the 1:1 complex may be estimated in two ways. First, they may be obtained directly from a plot of log k_c *vs.* $1/T$ using the values of k_c listed in Table IV. A second approach utilizes initial slopes of plots of k_{obsd}/k_u *vs.* $[D]_0$. Rearrangement of eq. 6 leads to

$$k_{obsd} = \frac{k_u}{1 + K_T[D]_0} + \frac{k_cK_T[D]_0}{1 + K_T[D]_0} \qquad (7)$$

which simplifies, under conditions where $K_T[D]_0 << 1$, to

$$k_{obsd} = k_u + k_cK_T[D]_0 \qquad (8)$$

Plots of k_{obsd} or k_{obsd}/k_u *vs.* $[D]_0$ are approximately linear at low $[D]_0$ and show gentle regular downward curvature at higher $[D]_0$ as predicted by eq. 7. It is apparent that if the proposed mechanism is correct, initial slopes of the k_{obsd}/k_u *vs.* $[D]_0$ plots are equal to k_cK_T/k_u. A plot of log (initial slope) *vs.* $1/T$ therefore leads directly to $(\Delta H_c^{\pm} + \Delta H° - \Delta H_u^{\pm})$ and to $(\Delta S_c^{\pm} + \Delta S° - \Delta S_u^{\pm})$, where the subscripts c and u refer to complexed and uncomplexed, as before. Combination with the quantities $\Delta H_u^{\pm}$, $\Delta S_u^{\pm}$, $\Delta H°$, and $\Delta S°$, which have already been directly determined (Tables II and III), leads to $\Delta H_c^{\pm}$ and $\Delta S_c^{\pm}$.

Results of the two analyses are summarized in Table V. It is apparent that the two estimates of $\Delta H_c^{\pm}$ and $\Delta S_c^{\pm}$ are in excellent agreement. In spite of fairly large uncertainties in k_c it seems safe to conclude that the 1:1 complex is more reactive in acetolysis principally because of a higher (more positive) entropy of activation (see Discussion, however).

Discussion

Significance of K_T from Kinetic Data.—Orgel and Mulliken[17] have discussed the spectrophotometric study of molecular complex formation in solution with respect to complications resulting from the formation of several geometrically and/or electronically different 1:1 complexes and to charge-transfer absorption resulting from random encounters between donor and acceptor. They showed that if two or more 1:1 complexes should be formed, the spectrophotometric method measures a total equilibrium constant, K (measured) $= \sum_i K_i$ (where K_i is the equilibrium constant for formation of the ith complex), and a weighted extinction coefficient, $\epsilon_\lambda^{D\cdot A}$ (measured) $= \sum_i K_i\epsilon_\lambda^i/K$ (where ϵ_λ^i is the extinction coefficient of the ith complex).

Exactly parallel arguments can be applied to the kinetic method used in the present work. Thus, if two or more 1:1 complexes are formed, equation 2 becomes

$$\frac{-d[ROTs]_0}{dt} = k_u[ROTs] + \sum_i k_i[ROTs\cdot D]_i$$
$$= k_u\{[ROTs]_0 - \sum_i [ROTs\cdot D]_i\} + \sum_i k_i[ROTs\cdot D]_i \qquad (9)$$

where $[ROTs\cdot D]_i$ is the concentration of the ith 1:1 complex and k_i its specific rate. The equilibrium constant for formation of each 1:1 complex (under conditions where $\{\sum_i [ROTs\cdot D]_i + \sum_i [ROAc\cdot D]_i\} << [D]_0$) is given by

$$K_i = \frac{[ROTs\cdot D]_i}{\{[ROTs]_0 - \sum_i [ROTs\cdot D_i]\}[D]_0} \qquad (10)$$

(17) L. E. Orgel and R. S. Mulliken, *ibid.*, **79**, 4839 (1957); see also, ref. 7b, footnote 2.

and the total equilibrium constant, K, by

$$K = \sum_i K_i = \frac{\sum_i [\mathrm{ROTs{\cdot}D}]_i}{\{[\mathrm{ROTs}]_0 - \sum_i [\mathrm{ROTs{\cdot}D}]_i\}[\mathrm{D}]_0} \quad (11)$$

Rearrangement of eq. 11 leads to

$$(\sum_i [\mathrm{ROTs{\cdot}D}]_i)/[\mathrm{ROTs}]_0 = F_c = K[\mathrm{D}]_0/(1 + K[\mathrm{D}]_0) \quad (12)$$

Defining a weighted average rate constant, k_i', for reaction of the complexes, such that $k_i' = (\sum_i K_i k_i)/K$, eq. 9 becomes

$$-\mathrm{d}[\mathrm{ROTs}]_0/\mathrm{d}t = k_u\{[\mathrm{ROTs}]_0 - \sum_i [\mathrm{ROTs{\cdot}D}]_i\} + k_i' \sum_i [\mathrm{ROTs{\cdot}D}]_i \quad (13)$$

Dividing by $[\mathrm{ROTs}]_0$ we obtain

$$k_{obsd} = k_u(1 - F_c) + k_i' F_c \quad (14)$$

Combination of eq. 12 and 14 with elimination of F_c leads to

$$\frac{1}{k_{obsd} - k_u} = \frac{1}{k_i' - k_u} + \frac{1}{K[\mathrm{D}]_0 (k_i' - k_u)} \quad (15)$$

Thus, it is apparent that K_T obtained from a plot of $1/(k_{obsd} - k_u)$ *vs.* $1/[\mathrm{D}]_0$ (intercept/slope) is a total equilibrium constant for formation of all 1:1 complexes and that k_c (measured), or k_i', is a weighted average rate constant for all 1:1 complexes.

It follows, therefore, that the agreement between the kinetic and spectrophotometric K_T's does not mean that the 1:1 complex (or complexes) responsible for the enhancement in optical density is the same complex (or complexes) producing rate enhancement. It is possible that one or more complexes are formed which are *less* reactive in acetolysis than uncomplexed *p*-toluenesulfonate.

If two or more 1:1 complexes with different enthalpies of formation are present, a plot of $\log K_T$ *vs.* $1/T$ should show curvature.[17] The present results provide no evidence for any such curvature, although considerable curvature could be obscured by the experimental uncertainties involved. It seems almost certain that at least two geometrically different 1:1 complexes are formed since the trinitrofluorenyl ring system in the reactant has two nonequivalent faces. Some evidence on this question may be obtained from studies, in progress, of the effects of charge-transfer complexing on the stereochemistry of acetolysis in this system.

Activation Parameters.—The trends in the apparent activation parameters (Table II) are consistent with the proposal that, as the donor concentration is increased, an increasing fraction of the acetolysis (*ca.* 72% at 0.05 *M* phenanthrene and *ca.* 80% at 0.08 *M* phenanthrene) is taking place by a path which requires a molecule of phenanthrene and a molecule of reactant to come together.[18] As the donor concentration is increased, $\Delta H^{\pm}$ apparent and $\Delta S^{\pm}$ apparent should both decrease, the minimum possible values of these quantities being $\Delta H_c^{\pm} + \Delta H^{\circ}$ and $\Delta S_c^{\pm} + \Delta S^{\circ}$, respectively.[19] Thus $\Delta H^{\pm}$ apparent should approach a value of about 21.5 to 21.1 kcal. mole^{-1} and $\Delta S^{\pm}$ apparent a value of about -16.4 to -17.5 e.u. mole^{-1}. Examination of the numbers in Table II shows this to be the case.

The activation parameters for acetolysis of the 1:1 complex, $\Delta H_c^{\pm}$ and $\Delta S_c^{\pm}$, indicate that the rate enhancement is an entropy effect, *i.e.*, that the complexed transition state has a lower standard free energy than the uncomplexed transition state because of a higher entropy. It is possible that the neighboring donor molecule reduces the extent of ordering of solvent molecules in the transition state.[20]

The possibility that part of the rate enhancement is a result of random encounters between reactant and donor places the significance of $\Delta H_c^{\pm}$ and $\Delta S_c^{\pm}$, as obtained in the present analysis, in some doubt. Orgel and Mulliken[17] have shown that, in spectrophotometric studies of complex formation, charge-transfer absorption resulting from random encounters ("contact charge transfer absorption") does not affect the measured value of the equilibrium constant but results in overestimation of the extinction coefficient of the 1:1 complex. They have suggested that "contact charge-transfer absorption" is responsible for apparent increases in $\epsilon_\lambda^{D\cdot A}$ with increasing temperature for trinitrobenzene–aniline and trinitrobenzene–naphthalene complexes.[21] In the present work it is impossible to say with certainty whether $\epsilon_\lambda^{D\cdot A}$ increases with temperature or not. In the kinetic estimation of K_T, exactly parallel arguments lead to the conclusion that rate enhancements arising from random encounters will have no affect on the measured value of K_T but will result in overestimation of k_c. Further, as the temperature increases (and K_T decreases) an increasing proportion of the apparent k_c would then be a result of chance encounters. Overestimation of the temperature dependence of k_c (measured by $\Delta H_c^{\pm}$) would result which, together with the overestimation of k_c at 70.0°, would lead to a value of $\Delta S_c^{\pm}$ (70.0°) which is too high. We are presently extending these studies to 2,4,5,7-tetranitro-9-fluorenyl *p*-toluenesulfonate (where random encounters are expected to be proportionately less important) and to several dinitro-9-fluorenyl *p*-toluenesulfonates (where random encounters are expected to be proportionately more important) in order to learn more about the importance of random encounters.

Characterization of the Transition States for Acetolysis.—Using a line of thought recently developed by Kurz,[22] information of a quantitative nature regarding the transition states for acetolysis of I can be gained from k_u, k_c, and K_T or, more directly, from the initial slopes of the plots of k_{obsd}/k_u *vs.* $[\mathrm{D}]_0$. The proposed mechanism may be reformulated to include equilibrium between initial and transition states as

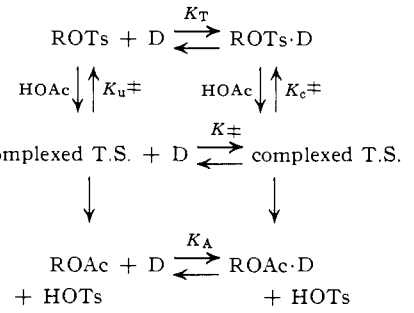
(18) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., Inc., New York, N. Y., 1959, p. 181.

(19) In order to approach these minimum values, K_T would have to be small (a major fraction of the reactant uncomplexed) and k_c large (a major fraction of the acetolysis proceeding through the 1:1 complex transition state).

(20) The entropy of activation has been used as a criterion for anchimeric assistance in acetolysis and formolysis of 2-arylethyl esters [S. Winstein and R. Heck, *J. Am. Chem. Soc.*, **78**, 4801 (1956)]. In these cases, as in the present case, an increase in $\Delta S^{\pm}$ reflects increased dispersal of charge in the transition state.

(21) Private communication from S. D. Ross, quoted in ref. 17.

(22) J. L. Kurz, *J. Am. Chem. Soc.*, **85**, 987 (1963).



If the concentrations of the transition states are at their equilibrium values with respect to reactants, and equilibrium exists between complexed and uncomplexed reactant, then the concentrations of uncomplexed and complexed transition states are at their equilibrium values with respect to one another, even though there is no direct equilibrium between them. From the transition state theory, assuming transmission coefficients close to unity, we can write[22]

$$k_u = (kT/h)K_u^{\pm};\quad k_c = (kT/h)K_c^{\pm}$$

However, $K_c^{\pm}K_T = K_u^{\pm}K_{\pm}$; hence,

$$k_c/k_u = K_c^{\pm}/K_u^{\pm} = K_{\pm}/K_T;\quad K_{\pm} = k_c\,K_T/k_u$$

The quantity $K_{\pm}$, the "virtual equilibrium constant"[22] for 1:1 complex formation between uncomplexed transition state and phenanthrene, is therefore just the initial slope of a plot of k_{obsd}/k_u *vs.* $[D]_0$ (see above). Thus, it is apparent that the uncomplexed transition state is an exceptionally good acceptor, having a virtual equilibrium constant for 1:1 complex formation with phenanthrene at 55.85° of about 55 l. mole^{-1} compared to about 3 l. mole^{-1} for the initial state.

Experimental

Materials.—Phenanthrene (Eastman Kodak White Label) was recrystallized from 95% ethanol. All samples were analyzed spectrophotometrically for anthracene, utilizing the 378 mμ absorption of anthracene. Anthracene was removed by treatment with maleic anhydride in boiling xylene, followed by crystallization from 95% ethanol. Phenanthrene used in the spectrophotometric studies contained 0.16% or less anthracene; that used in the kinetic studies contained 0.0062% or less anthracene.

2,4,7-Trinitro-9-fluorenyl *p*-toluenesulfonate, m.p. 208–210°, was prepared as previously described.[14]

Anhydrous acetic acid used in the spectrophotometric and kinetic studies was prepared from Baker and Adamson Reagent Grade acetic acid by distillation, analysis for water using Karl Fischer reagent, addition of the theoretical quantity plus 0.02 *M* freshly fractionated acetic anhydride, and heating near the reflux temperature for about 12 hr.

Standard sodium acetate solution (*ca.* 0.01 *M*) was prepared by dissolving a weighed quantity of reagent grade sodium carbonate, dried for at least 24 hr. at 100°, in distilled glacial acetic acid.

Kinetic Measurements.—Weighed amounts of *p*-toluenesulfonate ester (limited by its solubility to about 0.001 mole) and phenanthrene were added to a 500-ml. volumetric flask, dissolved with warming in a smaller volume of anhydrous acetic acid, cooled, and the solution was diluted to a volume of 500 ml. at 25° with anhydrous acetic acid. Samples of approximately 30-ml. volume were sealed in ampoules (8 in. Pyrex test tubes) and placed in the temperature bath. The reaction was followed by withdrawing ampoules at intervals of time, cooling to 25°, and titrating a 25.0-ml. aliquot with standard 0.01 *M* sodium acetate in glacial acetic acid. End points were determined potentiometrically using a Beckman Model 76 expanded scale pH meter with a glass electrode. Uncertainties in end point determinations are estimated to be about ±0.01 ml. The use of a visual indicator is prevented by the yellow-orange color of the rate solutions containing donor. In all of the operations involved in the kinetic measurements and during the rate run it is necessary to protect the reaction from light since the reaction is subject to photocatalysis.

Rate constants were calculated by means of the expression

$$k = \frac{2.303}{t}\log\frac{V_\infty - V_0}{V_\infty - V_t}$$

where V_0, V_t, and V_∞ are, respectively, volumes of standard base consumed at zero time (after thermal equilibration), time t, and after at least ten half lives. Infinity titers were averages of two or three values and in all cases were between 98 and 100% of theory. The rate constants are listed in Table I as averages of 6 to 10 values from a single rate run, with average deviations.

Activation parameters in the absence of phenanthrene and apparent activation parameters at 0.05 *M* phenanthrene were obtained as follows: Values of Arrhenius activation energies, E_a, were obtained by least squares analyses of plots of log k_{obsd} *vs.* $1/T$. Values of $\Delta H^{\pm}$ and $\Delta S^{\pm}$ were calculated from the equations $\Delta H^{\pm} = E_a - RT$ and $k = \frac{RT}{Nk}e^{\Delta S^{\pm}/R}e^{-\Delta H^{\pm}/RT}$. Standard deviations in E_a, $\Delta H^{\pm}$, and $\Delta S^{\pm}$ were calculated in the usual way[23] and reflect only scatter in the plot of log k_{obsd} *vs.* $1/T$ and not uncertainties in the values of k_{obsd}.

Spectrophotometric Determination of K_T.—Optical density measurements were carried out with a Beckman Model DU spectrophotometer equipped with a double set of thermospacers connected to a circulating constant temperature bath. The temperature of the cell compartment was held in this way to ±0.2° of the specified temperature. Samples of the *p*-toluenesulfonate were weighed directly into 50-ml. volumetric flasks, an aliquot of a stock solution of phenanthrene in glacial acetic acid was added, and the solution diluted to the mark with glacial acetic acid at 25°. Concentrations of *p*-toluenesulfonate varied from 5.96×10^{-4} to 1.32×10^{-3} *M* (35°); concentrations of phenanthrene varied from 2.34×10^{-2} to 7.92×10^{-2} *M* (35°). The blank cell was filled with a solution of phenanthrene in glacial acetic acid, identical in concentration with the unknown. A total of 13 measurements was carried out at 35°, 12 at 45°, and 8 at 55°. Optical density measurements were carried out at 10-mμ intervals between 380 and 450 mμ, but the data at 390 and 400 mμ led to values of K_T and $\epsilon_\lambda^{D\cdot A}$ having the smallest standard deviations. Optical densities did not change appreciably during the course of the measurements, indicating that no appreciable acetolysis or other light-induced reactions took place. Values of K_T and $\epsilon_\lambda^{D\cdot A}$ listed in Table III were obtained from least squares fits of plots of $[A]^\circ/(E_\lambda - \epsilon_\lambda^{A}[A]_0)$ *vs.* $1/[D]_0$ (see text for definitions of symbols) and are listed with their standard deviations, calculated in the usual way.[23] The average values of K_T are weighted averages (weighting factor = std. dev.$^{-2}$) and are listed with their standard deviations. Values of ϵ_λ^{A} at 390 and 400 mμ used in these calculations were averages of four separate determinations.

The ratio of stoichiometric donor concentration to stoichiometric acceptor concentration varied from about 23 to about 93. If K_T is in the neighborhood of 5 l. mole^{-1} or smaller, it can be readily shown[24] that at all combinations of acceptor and donor employed in the present study, errors in K_T resulting from the use of the Ketelaar equation (1)[15] rather than a more general and exact equation[25] cannot exceed about 1%.

The enthalpy of complex formation was obtained from the least squares slope of a plot of log K_T *vs.* $1/T$ and the entropy of complex formation from the expression: $\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T$, where $\Delta G^\circ = -RT \ln K_T$.

Analysis of Kinetic Data to Obtain K_T and k_c.—The kinetic data were analyzed according to eq. 6 using a weighted least squares procedure[23] in which values of $1/(k_{obsd} - k_u)$ were weighted in proportion to the reciprocal of the square of their standard deviations and values of $1/[D]_0$ were treated as exact. A simple least squares analysis is incorrect since uncertainties in $1/(k_{obsd} - k_u)$ differ widely, increasing sharply as k_{obsd} approaches k_u. Standard deviations in values of k_{obsd} and k_u were calculated using the formula

$$S_k = (\Sigma d^2/n)^{1/2}$$

where d is the deviation of each individual rate constant (de-

(23) L. G. Parratt, "Probability and Experimental Errors in Science," John Wiley and Sons, Inc., New York, N. Y., 1961.

(24) M. Tamres, *J. Phys. Chem.*, **65**, 654 (1961).

(25) N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, **81**, 6138 (1959).

termined from V_0, V_∞, and individual values of V_t and t) from the mean. This procedure is not strictly correct in that it assumes an equal uncertainty for all rate constants determined in a single run. However, the procedure is approximately correct if all rate constants are based on points taken between 20 and 80% reaction, and a rigorous treatment, if one were available, would not appreciably change the weighting factors and would have an even smaller effect on the best fit slopes and intercepts. The weighting factor, w, is given by the expression

$$w = (k_{obsd} - k_u)^4/(s^2_{k_{obsd}} + s^2_{k_u})$$

Activation Parameters for Acetolysis of the 1:1 Complex.—Least squares analysis of a plot of log k_c *vs.* $1/T$ led directly to ΔH_c and ΔS_c by the usual procedure (see above). Least squares analysis of a plot of $k_c k_u/K_T$ (initial slopes of plots of k_{obsd}/k_u *vs.* $[D]_0$) led to values for $(\Delta H_c^{\pm} + \Delta H^\circ - \Delta H_u^{\pm})$ and $(\Delta S_c^{\pm} + \Delta S^\circ - \Delta S_u^{\pm})$, together with standard deviations for these quantities. Combination with directly measured values of ΔH°, $\Delta H_u^{\pm}$, ΔS°, and $\Delta S_u^{\pm}$ led to $\Delta H_c^{\pm}$ and $\Delta S_c^{\pm}$. Standard deviations for the quantities were calculated in the usual way[23] from standard deviations in $(\Delta H_c^{\pm} + \Delta H^\circ - \Delta H_u^{\pm})$, ΔH°, and $\Delta H_u^{\pm}$.

Acknowledgment.—We wish to thank the National Science Foundation for a grant in support of this research.

[CONTRIBUTION NO. 3062 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIF.]

The Acid-Catalyzed Cyclization of Acyclic Dienes

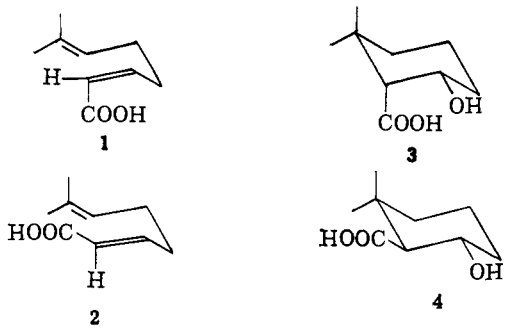
BY H. E. ULERY AND J. H. RICHARDS[1]

RECEIVED JANUARY 6, 1964

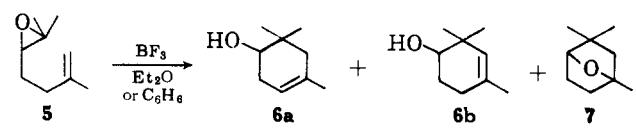
The acid-catalyzed cyclizations of *trans,trans*- and *cis,cis*-2,6-octadiene have been investigated utilizing deuterated acid to initiate cyclization. The stereochemistry of the products shows that the cyclization process is concerted with proton attack and follows the stereoelectronic predictions made for terpene biosynthesis. A small percentage of the time the acquisition of the nucleophile is clearly concerted with the preceding steps and leads, likewise, to the theoretically expected product.

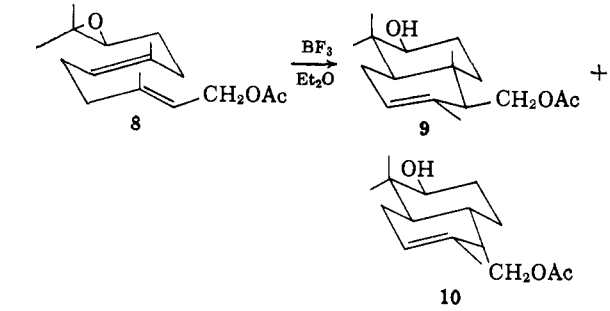
Introduction

The cyclization of acyclic polyolefins plays an important role in the biogenesis of many terpenoid compounds. For example, the cyclization of squalene to lanosterol[2] is an important step in the biosynthesis of cholesterol and other steroid hormones. The stereochemical implications of olefin cyclization have been elegantly discussed in a theoretical sense[3,4] and a large body of experimental studies on olefin cyclizations[5-8] has appeared. Though some of the systems studied gave those products expected to result from a concerted sequence of stereoselective events, these products could also have arisen by processes that were *not entirely* concerted, because it was not possible to examine the stereochemistry at *all* centers which were involved in the cyclization reaction, *i.e.*, had undergone rehybridization from sp^2 to sp^3. Another disadvantage with many of the systems studied hitherto is that they have utilized trisubstituted olefins which increase the possibility that classical carbonium ions might intervene as intermediates with resultant loss of stereospecificity. For example, the cyclization of *cis*- and *trans*-apogeranic acids (**1**) and (**2**) to the expected products **3** and **4**, respectively,[5,6] does not demand a totally concerted cyclization, but requires only a *trans* addition to the terminal double bond.



Recently, the cyclization of epoxy olefins has received some attention.[9-11] Goldsmith[9] studied the cyclization of geraniolene monoepoxide (**5**) by boron trifluoride in benzene and ether solvent and observed the formation of two isomers of 2,2,4-trimethylcyclohexenol (**6a** and **6b**) and 2,2,4-trimethyl-1,4-endoxycyclohexane (**7**) in small yield. van Tamelen, *et al.*,[10] studied the reaction of the terminal monoepoxide of *trans,trans*-farnesyl acetate (**8**) also with boron trifluoride–ether and were able, after extensive chromatographic purification, to isolate a modest yield of bicyclic diol monoacetate which consisted of 85% of stereoisomer **9** and 15% of its epimer **10**. Attempted[11] cyclizations of monoepoxides of a number of 1,5-dienes in protic solvents led almost exclusively





(1) Alfred P. Sloan Fellow.

(2) T. T. Tchen and K. Bloch, *J. Biol. Chem.*, **226**, 921 (1957).

(3) L. Ruzicka in "Perspectives in Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p. 265, *et seq.*

(4) J. B. Hendrickson, *Tetrahedron*, **7**, 82 (1959).

(5) R. Helg and H. Schinz, *Helv. Chim. Acta*, **35**, 2406 (1952).

(6) G. Gamboni, H. Schinz, and A. Eschenmoser, *ibid.*, **37**, 964 (1954).

(7) G. Stork and A. W. Burgstahler, *J. Am. Chem. Soc.*, **77**, 5068 (1955).

(8) P. A. Stadler, A. Nechvatel, A. J. Frey, and A. Eschenmoser, *Helv. Chim. Acta*, **40**, 1373 (1957).

(9) D. J. Goldsmith, *J. Am. Chem. Soc.*, **84**, 3913 (1962).

(10) E. E. van Tamelen, A. Storni, E. J. Hessler, and M. Schwartz, *ibid.*, **85**, 3295 (1963).

(11) H. Ulery, Ph.D. Thesis, California Institute of Technology, 1963.