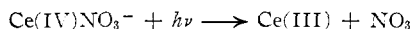


spectrum are broader than the gas phase spectrum by a factor of two or three as expected, they are in excellent agreement with the results of DeMore and Davidson⁵ in frozen matrix. This solution spectrum based on our assignments for the maxima of the two most prominent bands at 635 and 671 μ , shows only a slight solvent shift of about 10 μ when compared with the 623 and 663 μ band heads measured by Ramsay⁷ for the gas phase spectrum.

The estimated lifetime of the NO_3 radical is approximately 200 microseconds maximum in the aqueous nitric acid system. However, its apparent lifetime is noticeably shortened upon the addition of acetic acid to the medium. This decrease in NO_3 lifetime was shown to be related to the amounts of acetic acid added as were the yields of carbon dioxide and methane isolated from these photolyzed solutions. When the added acetic acid concentration is about 1.0 M , we are just barely able to detect the NO_3 radical with our present apparatus. A more accurate and comprehensive study of the NO_3 lifetime and its dependence on various solution parameters is now in progress.

Our method of forming the NO_3 radical makes it feasible to study its specific reactivity and to evaluate its possible synthetic uses as a new reagent for the nitration and oxidation of a given substrate. Further, we believe that such applications provide additional chemical evidence that the NO_3 radical is the probable reaction initiator in a variety of solvent systems. For example, we find that the photolysis of a solution containing 0.02 M ceric ammonium nitrate in glacial acetic acid gives rise to products whose yields as a function of temperature and light intensity are best explained by secondary radical displacement processes initiated by NO_3 radical formed in the primary photochemical step. The chemical data given here support this contention. The ceric salt is always reduced with the loss of one nitrate group from the original ion complex. The acetic acid is decomposed at high flash intensities to yield only carbon dioxide and methyl nitrate as the major observable products, with minor yields of methane, methanol, and methyl acetate. The decreased quantum yield of methane with increasing light intensities and the marked temperature independence of the methane yield definitely preclude the possibility that methyl radicals (derived, for instance, by the decomposition of prior acetoxy radicals) are a probable source of the methyl nitrate product in this system. The quantum yield for cerium reduction is found to be 0.36 at 30°, which shows the initiating reaction to be remarkably efficient and unusual when compared to other reported photoreductions of cerium.

On the basis of both the spectroscopic and chemical evidence cited and also because we have shown by spectrophotometric and electrophoresis studies that the most probable photoreactive ceric species necessary to generate the NO_3 radical are the $\text{Ce}(\text{NO}_3)_4$ molecule and the hexanitratocerate ion, $\text{Ce}(\text{NO}_3)_6^{--}$, we believe that the primary photochemical process most consistent with all the data in the systems we have studied can be represented as



whereby the absorbed quantum initiates an intramolecular oxidation-reduction reaction in the excited state of the absorbing species by means of an electron charge exchange between one of the closely coupled nitrate ions and its associated cerium(IV) atom. This action results in the formation of a cerium(III) species and the efficient release of a very reactive NO_3 radical which can then attack other components in the solution. The details of this specific attack on glacial acetic acid

and our interpretation of the ensuing reaction mechanism will be the subject of a subsequent publication.

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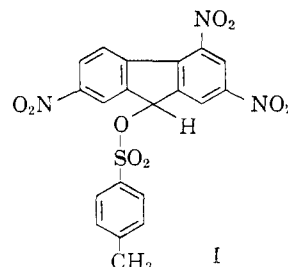
THOMAS W. MARTIN
ALAN HENSHALL
ROBERT C. GROSS

RECEIVED OCTOBER 18, 1962

ENHANCEMENT OF ACETOLYSIS RATES BY CHARGE-TRANSFER COMPLEXING¹

Sir:

We wish to report evidence that the reactivity of suitably constituted compounds can be strongly modified through charge-transfer complexing. Rates of acetolysis of 2,4,7-trinitro-9-fluorenyl *p*-toluenesulfo-



nate (I)² at 100° are increased by addition of aromatic donors in 0.02 M concentration (Table I).

TABLE I
EFFECT OF AROMATIC DONORS IN THE ACETOLYSIS OF 2,4,7-TRINITRO-9-FLUORENYL *p*-TOLUENESULFONATE^a

Donor	Temp., ^b °C.	10 ² [Donor], <i>M</i>	10 ² <i>k</i> ₁ , sec. ⁻¹
None	99.3	...	1.38 ± 0.04
None	99.9	...	1.86 ± 0.02
Hexamethylbenzene	99.3	2.02	2.08 ± 0.06
Hexamethylbenzene	99.9	1.86	2.50 ± 0.03
Hexaethylbenzene	99.9	1.85	1.79 ± 0.01
Phenanthrene	99.3	2.00	2.61 ± 0.13
Acenaphthene	99.3	2.01	7.05 ± 0.27
Anthracene	99.3	2.01	13.98 ± 1.07
Anthracene	99.9	0.200	3.18 to 2.61 ^c

^a Concentration of *p*-toluenesulfonate was 0.0020 M for all runs. ^b Temperatures were maintained at 99.3 ± 0.1° and 99.9 ± 0.02°. ^c Instantaneous first order rate constants showed a regular decrease over the range of the reaction studied (12 to 91%).

The results of a more detailed study involving phenanthrene-donor are summarized in Table II. Plots of

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

Temperature					
55.83 ± 0.01°		85.0 ± 0.01°		99.9 ± 0.02°	
10 ² [Donor], <i>M</i>	10 ² <i>k</i> ₁ , sec. ⁻¹	10 ² [Donor], <i>M</i>	10 ² <i>k</i> ₁ , sec. ⁻¹	10 ² [Donor], <i>M</i>	10 ² <i>k</i> ₁ , sec. ⁻¹
0	1.66 ± 0.03	0	4.44 ± 0.08	0	1.86 ± 0.02
0.971	2.56 ± 0.01	0.943	5.67 ± 0.06	0.931	2.36 ± 0.03
1.94	3.29 ± 0.09	1.89	7.04 ± 0.06	1.86	2.86 ± 0.02
3.89	4.99 ± 0.04	3.77	9.43 ± 0.12	3.72	3.61 ± 0.01
4.85	5.72 ± 0.09	5.66	11.57 ± 0.14	5.58	4.35 ± 0.03
5.82	6.33 ± 0.05				
6.79	7.05 ± 0.03				

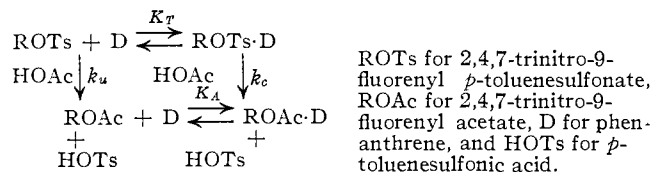
(1) A preliminary report of part of this work was presented before the Division of Organic Chemistry, 139th Meeting of the American Chemical Society, St. Louis, Mo., March 22, 1960 (Abstracts, p. 22-O).

(2) Allan K. Colter and Samuel S. Wang, *J. Org. Chem.*, **27**, 1517 (1962).

(7) D. A. Ramsay, private communication, April, 1962.

k vs. [Donor] are nearly linear with gentle downward curvature. Apparent activation parameters change from $\Delta H^\ddagger = 25.8$ kcal. mole⁻¹ and ΔS^\ddagger (85.0°) = -11.4 e.u. mole⁻¹, in the absence of donor, to $\Delta H^\ddagger = 22.9$ kcal. mole⁻¹ and ΔS^\ddagger (85.0°) = -17.8 e.u. mole⁻¹ at 0.05 *M* phenanthrene.

The simplest mechanism for incursion of charge-transfer complexes in the acetolysis reaction is:



The observed rate constant, k_{obs} , should then be given by the expression

$$k_{\text{obs}} = k_u F_u + k_c F_c \quad (1)$$

where F_u and F_c are the fractions of the *p*-toluenesulfonate uncomplexed and complexed, respectively, at any time. Strict first order behavior requires F_u and F_c to be constant throughout the course of the rate, a situation which will obtain if the total donor concentration, $[\text{D}]_0$ is $\gg \{[\text{ROTs}\cdot\text{D}] + [\text{ROAc}\cdot\text{D}]\}$ at all times, or if $K_A \approx K_T$. The first of these conditions is met in all cases except in one run involving anthracene donor (Table I) where, indeed, a regular decrease in k_{obs} with time was observed.

Combination of equation (1) with the equilibrium condition for formation of the phenanthrene-*p*-toluenesulfonate complex (again, under conditions where $[\text{D}]_0 \gg \{[\text{ROTs}\cdot\text{D}] + [\text{ROAc}\cdot\text{D}]\}$) leads to equation (2),³ an equation entirely analogous to the Ketelaar form⁴ of the Benesi-Hildebrand equation.⁵

$$\frac{1}{k_{\text{obs}} - k_u} = \frac{1}{k_o - k_u} + \frac{1}{K_T[\text{D}]_0(k_o - k_u)} \quad (2)$$

A plot of $1/(k_{\text{obs}} - k_u)$ vs. $1/[\text{D}]_0$ for the data at 55.85° is shown in Fig. 1. From these data,⁶ $K_T = 2.8$ liter mole⁻¹ and $k_c = 3.5 \times 10^6$ sec.⁻¹. K_T also was evaluated in the usual way⁴ from spectrophotometric measurements at 390 and 400 μ . Values of K_T at 25, 35 and 45° were, respectively, 7.7 ± 0.2 , 5.5 ± 0.1 and 4.1 ± 0.3 liter mole⁻¹, leading to an estimate of 3.0 liter mole⁻¹ for K_T at 55.85°, in excellent agreement with the kinetic value. The accuracy of these determinations is limited seriously by the low solubilities of both the *p*-toluenesulfonate (*ca.* 0.002 *M*) and phenanthrene (*ca.* 0.08 *M*) in glacial acetic acid. Insufficient kinetic data are available at 85.0 and 99.9° to make any reasonable estimates of K_T at these temperatures.

Our proposal that the rate enhancements are a result of charge-transfer complexing is supported by these observations: (i) The enhancements are sensitive to the nature of the donor and qualitatively parallel λ_{max} for charge transfer absorption with the acceptors trinitrobenzene,⁷ chloranil,⁸ and tetracyanoethylene.^{9,10}

(3) For a closely similar deviation, see R. M. Keefer, J. H. Blake, III, and L. J. Andrews, *J. Am. Chem. Soc.*, **76**, 3062 (1954).

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

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

(6) The data were analyzed using a weighted least squares treatment as described in L. G. Parratt, "Probability and Experimental Errors in Science," John Wiley and Sons, Inc., N. Y., 1961. A simple least squares treatment is incorrect because values of $1/(k_{\text{obs}} - k_u)$ differ widely in uncertainty. A simple least squares treatment of the four points corresponding to the highest donor concentration gives $K_T = 3.4$ (std. dev. 0.3).

(7) M. J. S. Dewar and A. R. Lepley, *J. Am. Chem. Soc.*, **83**, 4560 (1961).

(8) S. Winstein, unpublished results.

(9) (a) R. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958). (b) M. J. S. Dewar and A. R. Lepley, *ibid.*, **84**, 395 (1962).

(10) A quantitative correlation must await evaluation of k_o for a series of donors.

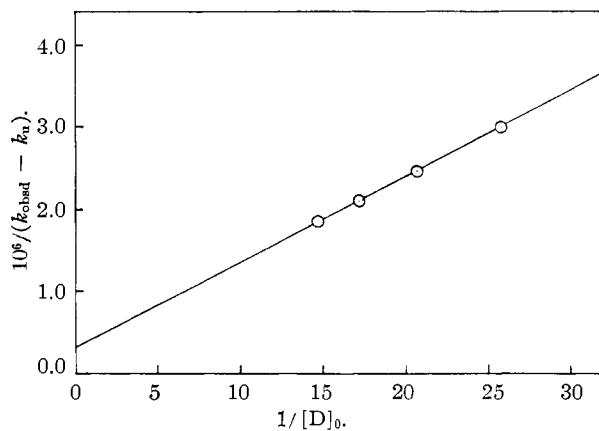


Fig. 1.

(ii) Hexaethylbenzene, in contrast to hexamethylbenzene, produces no rate enhancement.¹¹ (iii) When $[\text{D}]_0 \approx [\text{ROTs}]$ at zero time, first order rate constants show a regular drift. (iv) Values of K_T determined spectrophotometrically and kinetically are in excellent agreement.

The observation that $k_c > k_u$ ($k_c/k_u = 21$) is as expected since the electronically-deficient activated complex should form a stronger complex than the ground state. Studies presently underway are aimed at defining the scope of such rate enhancements,¹² the relationship between k_c and the structure of the donor, and the stereochemical consequences of charge-transfer involvement in solvolysis reactions.

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

(11) There have been numerous references to the relative ineffectiveness of hexaethylbenzene as a donor; see, for example, ref. 9a.

(12) In this connection it is interesting that B. B. Smith and J. E. Leffler, *J. Am. Chem. Soc.*, **77**, 2059 (1955), obtained no convincing evidence for enhancement of the rate of solvolysis of *p*-nitrobenzhydryl bromide by complex formation in aqueous acetone.

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MECHANISM OF THE THERMAL ISOMERIZATION OF 5-NORBORNENE-2,3-endo-DICARBOXYLIC ANHYDRIDE¹

Sir:

The thermal interconversions of α - and β -1-hydroxy-dicyclopentadiene with *syn*- and *anti*-8-hydroxydicyclopentadiene, respectively, with retention of optical activity² and analogous rearrangements^{3,4} have been considered in mechanistic descriptions of the Diels-Alder reaction.²⁻⁵ In the case of deuterium-labeled methacrolein dimer, an internal stereospecific pathway for rearrangement and complete dissociation of the dimer are very much in competition at 180°, and both reactions occur simultaneously. As was noted,⁴ the possibility that different energy paths are involved in the two processes remained unsettled.

5-Norbornene-2,3-endo-dicarboxylic anhydride (I) is thermally isomerized to the *exo*-isomer at 190°. This rearrangement takes place by both an internal

(1) Supported in part by the National Science Foundation.

(2) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

(3) P. Yates and P. Eaton, *ibid.*, **12**, 13 (1961); R. C. Cookson, J. Hudcok and R. O. Williams, *Tetrahedron Letters*, No. 22, 29 (1960).

(4) R. P. Lutz and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 2198 (1961).

(5) M. J. S. Dewar, *Tetrahedron Letters*, No. 4, 16 (1959); R. B. Woodward and T. J. Katz, *ibid.*, No. 5, 19 (1959); J. A. Berson and A. Remanick, *J. Am. Chem. Soc.*, **83**, 4947 (1961); J. A. Berson, A. Remanick and W. A. Mueller, *ibid.*, **82**, 5501 (1960).

(6) D. Craig, *ibid.*, **73**, 4889 (1951).