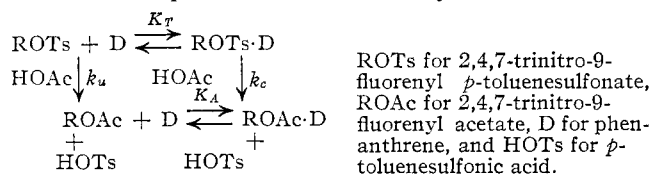


k vs. [Donor] are nearly linear with gentle downward curvature. Apparent activation parameters change from $\Delta H^\ddagger = 25.8$ kcal. mole⁻¹ and $\Delta S^\ddagger$ (85.0°) = -11.4 e.u. mole⁻¹, in the absence of donor, to $\Delta H^\ddagger = 22.9$ kcal. mole⁻¹ and $\Delta S^\ddagger$ (85.0°) =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

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

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_c for a series of donors.

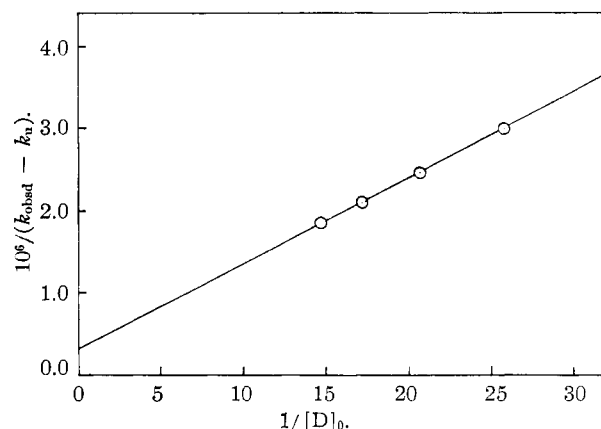


Fig. 1.

(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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RECEIVED NOVEMBER 8, 1962

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).

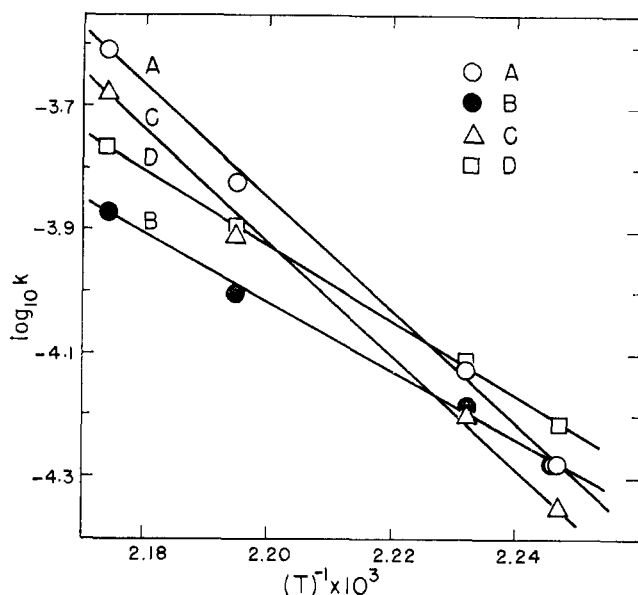


Fig. 1.—Arrhenius plots of first-order rate constants for the internal and external rearrangement of 5-norbornene-2,3-endo-dicarboxylic anhydride: A, k_{ext} , uncorrected; B, k_{int} , uncorrected; C, k_{ext} , with 15% correction (see text); k_{int} , with 15% correction.

mechanism and dissociation-recombination of addends.⁷ The internal route for isomerization may be related to the dissociation-recombination, and hence pertinent to mechanistic representations of the Diels-Alder reaction.^{6,7}

We now report evidence which seems to indicate that the two mechanisms for thermal rearrangement of 5-norbornene-2,3-endo-dicarboxylic anhydride involve different energy paths.

Rearrangement of the *endo*-anhydride (I) in decalin solution in the presence of tetracyanoethylene gave 2,2,3,3-tetracyanonorborn-5-ene from cyclopentadiene produced by dissociation on the external path(s) as well as *exo*-anhydride from the internal route. The ratio of 2,2,3,3-tetracyanonorborn-5-ene to 5-norbornene-2,3-*exo*-dicarboxylic anhydride was determined by integration of the n.m.r. spectrum of the mixture of these two products and unrearranged *endo*-anhydride and found to be markedly temperature dependent; 1.72 ± 0.05 at 185° , 1.07 ± 0.03 at 174° , 0.63 ± 0.03 at 160° .

A kinetic study of the rearrangement of the *endo*-anhydride to the *exo*-isomer in decalin solution in the absence of tetracyanoethylene led to first-order rate constants for the conversion: $k(\text{sec}^{-1}) \times 10^5 = 38 \pm 3$ at 187° , 25 ± 2 at 182.5° , 14 ± 1 at 175° and 10.6 ± 1 at 172° .

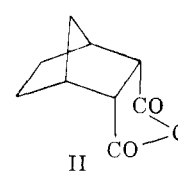
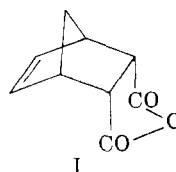
By assuming that tetracyanoethylene reacts much faster than maleic anhydride throughout the temperature range in question⁸ and that all the cyclopentadiene-tetracyanoethylene adduct stems from the *endo*-anhydride, calculation gives Arrhenius activation energies and pre-exponential factors for the internal and external processes: $E_{\text{ext}} = 42 \text{ kcal. mole}^{-1}$, $E_{\text{int}} = 25 \text{ kcal. mole}^{-1}$, $A_{\text{ext}} = 10^{16} \text{ sec}^{-1}$, $A_{\text{int}} = 10^{9.8} \text{ sec}^{-1}$.

(7) J. A. Berson and R. D. Reynolds, *J. Am. Chem. Soc.*, **77**, 4434 (1955); J. A. Berson, R. D. Reynolds and W. M. Jones, *ibid.*, **78**, 6049 (1956).

(8) (a) Cf. J. A. Berson and W. A. Mueller, *ibid.*, **83**, 4940 (1961); (b) The possibility that any significant amount of *exo*-maleic anhydride adduct arises by dissociation of the tetracyanoethylene adduct after the latter is formed, was ruled out by control experiments. At 195° in decalin, about 7% of maleic anhydride adduct was formed by heating the tetracyanoethylene adduct in the presence of excess maleic anhydride for 35 min. When the tetracyanoethylene adduct was heated with tetracyanoethylene and maleic anhydride in 1.2 molar proportions, the yield of maleic anhydride adduct dropped to 2%.

The second assumption ignores the fact that some of the cyclopentadiene-tetracyanoethylene adduct stems from the *exo*-anhydride first formed through the internal mechanism. Since the kinetic data for rearrangement in the absence of tetracyanoethylene exhibited first-order behavior until 40–50% conversion and the rearrangements in the presence of tetracyanoethylene were carried to 50–70% conversion, the proportion of 2,2,3,3-tetracyanonorborn-5-ene formed from the *exo*-anhydride cannot be large. This uncertainty prohibits calculation of reliable values for entropies and energies of activation, but it does not obscure the basic results. For instance, if 15% of the 2,2,3,3-tetracyanonorborn-5-ene came from the *exo*-anhydride, the data would lead to $E_{\text{ext}} = 42 \text{ kcal. mole}^{-1}$, $E_{\text{int}} = 28 \text{ kcal. mole}^{-1}$, $A_{\text{ext}} = 10^{16} \text{ sec}^{-1}$, $A_{\text{int}} = 10^{9.7} \text{ sec}^{-1}$. With or without a correction for this second external path, the calculated first-order rate constants for the internal and external rearrangement of the *endo*-anhydride give good straight lines in Arrhenius plots (Fig. 1) and the estimated kinetic parameters for the two processes are quite dissimilar.

Further, 2,3-*endo*-norbornanedicarboxylic anhydride (II) was converted to the extent of $22 \pm 2\%$ to its *exo*-isomer when heated to 250° for 24 hours. Since the ring system of I is likely to be more strained than that of II, it should be labile to rearrangement under relatively less severe conditions.



In view of the widely different energetic parameters characterizing the two processes, and of the thermal rearrangement of 2,3-*endo*-norbornanedicarboxylic anhydride to its *exo*-isomer at 250° , we regard as remote the possibility that the two pathways for thermal isomerization of I are closely related.

This work suggests that kinetic studies with systems capable of interconversions similar to those shown by the 1-hydroxycyclopentadienes may clarify the relationship of these rearrangements with Cope rearrangements^{2–5} and Diels-Alder reactions.

More detailed investigations of mechanisms of the thermal isomerization of I to its *exo*-isomer will be reported later.

We thank Professor J. A. Berson for his helpful interest and suggestions regarding this study.

(9) National Science Foundation Predoctoral Fellow, 1960–1962; Department of Chemistry, University of Illinois, Urbana, Illinois.

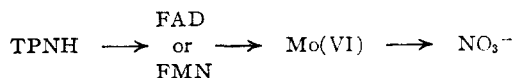
CONTRIBUTION No. 2907
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RECEIVED NOVEMBER 15, 1962

PHOTOCHEMICAL REDUCTION OF NITRATE CATALYZED BY MOLYBDENUM(VI) AND FLAVIN MONONUCLEOTIDE

Sir:

The biological reduction of nitrate to nitrite, catalyzed by the molybdoflavoenzyme nitrate reductase, has been indicated to proceed through the following sequence of electron transfers¹



(1) D. J. D. Nicholas and A. Nason, *J. Biol. Chem.*, **211**, 183 (1954).