Chemical Behavior of Charge-Transfer Complexes. V. Catalysis of Acetolysis of 2,4,7-Trinitro-9-fluorenyl *p*-Toluenesulfonate by Methoxynaphthalene and Dimethoxynaphthalene Donors[1]

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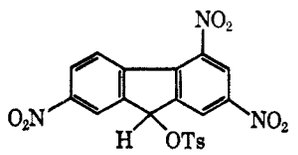
To investigate the effect of donor structure on catalysis by charge-transfer complexing in acetolysis reactions, rates of acetolysis of 2,4,7-trinitro-9-fluorenyl *p*-toluenesulfonate were measured at 85.30° in the presence of a series of donor concentrations for each of nine naphthyl ether donors. The donors examined included 1- and 2-methoxynaphthalene and 1,4-, 1,5-, 1,6-, 1,7-, 2,3-, 2,6-, and 2,7-dimethoxynaphthalene. For all of these donors except 1,4-dimethoxynaphthalene the data were analyzed to obtain rate constants, k_c, for acetolysis of the 1:1 donor–*p*-toluenesulfonate complexes, and equilibrium constants, K, for 1:1 substrate–donor complexation. The reactivities of the 1:1 complexes in acetolysis varied from 26 times as great as uncomplexed *p*-toluenesulfonate with 2-methoxynaphthalene to 1.9×10^3 times as reactive with 1,5-dimethoxynaphthalene. Attempts to correlate the catalytic effectiveness of these donors with their highest occupied molecular orbital energies calculated by the Hückel method were partially successful. 2,3-Dimethoxynaphthalene was studied at 64.8° as well; the 1:1 complex in this case is more reactive than uncomplexed substrate because of a more favorable entropy of activation. Wavelengths of the first charge-transfer maxima for complexes of the nine naphthyl ether donors with the acceptors tetracyanoethylene and chloranil were measured in methylene chloride. Reasonably good linear correlations were obtained between the frequencies of these maxima and the calculated highest occupied molecular orbital energies.

The initial report of catalysis by aromatic donors in acetolysis of 2,4,7-trinitro-9-fluorenyl *p*-toluenesulfonate[2] (TNF-OTs) raised two interesting questions. The first of these, that of the structural requirements of the reactant, has been investigated in part and is the subject of the previous paper in this series.[1b] An equally interesting question is the relationship between the structure of the donor and its catalytic effectiveness.



TNF-OTs

Our early results[2] indicated that observed rate enhancements were highly sensitive to donor structure. For example, at 99.3° 0.02 *M* anthracene produced an 8.61-fold increase in the rate of acetolysis of TNF-OTs while 0.02 *M* phenanthrene produced a 1.60-fold increase. The observed rate enhancements produced by phenanthrene, acenaphthene, and anthracene qualitatively paralleled λ_{max} for charge-transfer absorption of complexes of these donors with trinitrobenzene, chloranil, and tetracyanoethylene. Our aim in the present work was to investigate in more detail the relationship between donor catalytic effectiveness and structure.

The assumed mechanism[2] of the catalysis follows.

$$\text{ROTs} + \text{D} \underset{}{\overset{K}{\rightleftharpoons}} \text{ROTs}\cdot\text{D}$$

$$\text{HOAc} \downarrow k_u \qquad \text{HOAc} \downarrow k_c$$

products products

ROTs, D, and ROTs·D are substrate, donor, and 1:1 complex, respectively; K is the equilibrium constant for 1:1 complex formation; k_u and k_c are rate constants for acetolysis of uncomplexed and complexed substrate, respectively. The observed rate constant in the presence of donor is therefore a function of both K and k_c. The former is expected to be sensitive to steric influences,[3] including coplanarity of the donor, as well as symmetry and rigidity of the donor. Initially it was felt that k_3 should be more directly related to the usual experimental measures of donor strength such as positions of charge-transfer maxima, and theoretical quantities such as the highest occupied molecular orbital energies (see below, however).

Only a very few unsubstituted polynuclear aromatic hydrocarbons are sufficiently soluble in glacial acetic acid for reasonably accurate determinations of k_c and K to be made. For this reason, we looked to substituted aromatics and chose for the first study a series of nine methoxynaphthalene (MN) and dimethoxynaphthalene (DMN) donors. Although very similar in structure, significant variation in donor properties was expected within this series of compounds. A complicating feature of ether donors is the possibility of direct nucleophilic participation by oxygen in the substitution transition state. Such participation would, of course, make any comparison of catalytic effectiveness with calculated π-electron energies or experimental quantities depending mostly on π-electron energies meaningless.

The methoxybenzenes have been extensively studied as π donors.[4,5] Zweig[4] has had some success in correlating charge-transfer transition energies of complexes involving methoxybenzene donors with the highest occupied molecular orbital (HOMO) coefficients of these donors calculated by the Hückel molecular orbital (HMO) method. This type of correlation has been demonstrated for arylamines as well.[6] Since no similar correlation had been reported for the methoxy- and dimethoxynaphthalenes, and since some

(1) (a) Abstracted from the Ph.D. Thesis of S. H. Hui, Carnegie Institute of Technology, Sept 1966. (b) Part IV of this series: A. K. Colter, F. F. Guzik, and S. Hui, *J. Amer. Chem. Soc.*, **88**, 5754 (1966).

(2) A. K. Colter and S. S. Wang, *ibid.*, **85**, 114 (1963).

(3) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964.

(4) (a) A. Zweig, *J. Phys. Chem.*, **67**, 506 (1963); (b) A. Zweig, J. E. Lehnsen, and M. A. Murray, *J. Amer. Chem. Soc.*, **85**, 3933 (1963).

(5) E. M. Voigt, *ibid.*, **86**, 3611 (1964).

(6) M. Nepraš and R. Zahradnik, *Collect. Czech. Chem. Commun.*, **29**, 1555 (1964).

TABLE I

FIRST CHARGE-TRANSFER MAXIMA FOR COMPLEXES OF METHOXY- AND DIMETHOXYNAPHTHALENES WITH TCNE AND CHLORANIL

		TCNE		Chloranil		Energy of HOMO[c]	
No.	Donor	λ_{max},[a] mμ	ν_{max}, KK	λ_{max},[a] mμ	ν_{max}, kK	Set i[c]	Set ii[d]
1	2-MN	613 (609)	16.3 (16.4)	540 (524)	18.5 (19.1)	0.581	0.556
2	1-MN	646	15.5	562	17.8	0.538	0.498
3	2,3-DMN	591	16.9	529 (525)	19.0 (19.0)	0.564	0.541
4	2,7-DMN	594	16.8	526 (519)	19.0 (19.3)	0.555	0.522
5	2,6-DMN	706	14.2	611	16.4	0.537	0.483
6	1,6-DMN	684 (681)	14.6 (14.7)	594	16.8	0.514	0.466
7	1,7-DMN	704	14.2	598	16.7	0.504	0.445
8	1,5-DMN	730	13.7	623	16.1	0.475	0.411
9	1,4-DMN	795	12.6	685	14.6	0.452	0.365

[a] Estimated uncertainty ±5 mμ for TCNE, ±10–15 mμ for chloranil. Values in parentheses are experimental maxima for cases where corrections were made for overlap with the second charge-transfer peak (see Experimental Section). [b] Coefficient m in the Hückel HOMO energy, $E = \alpha + m\beta$. [c] $\alpha_O = \alpha_C + 2.0\beta_{C-C}$, $\beta_{C-O} = 0.8\beta_{C-C}$. [d] $\alpha_O = \alpha_C + 2.0\beta_{C-C}$, $\beta_{C-O} = \beta_{C-C}$.

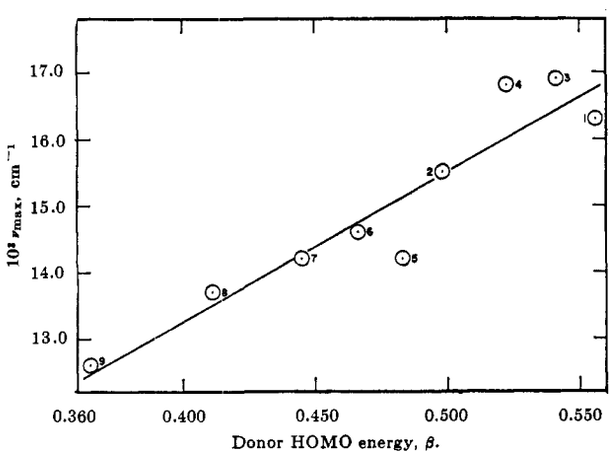


Figure 1.—Plot of charge-transfer frequencies *vs.* donor HOMO energies for complexes of naphthyl ether donors with TCNE.

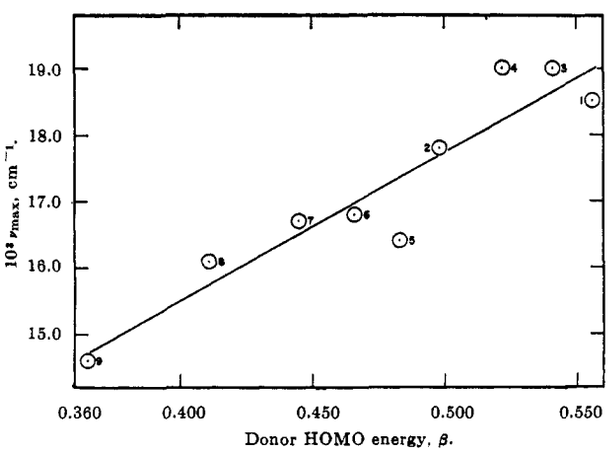


Figure 2.—Plot of charge-transfer frequencies *vs.* donor HOMO energies for complexes of naphthyl ether donors with chloranil.

experimental measure of donor strengths was desired, charge-transfer absorption maxima of complexes of these donors with chloranil and tetracyanoethylene (TCNE) were measured in methylene chloride as part of a complementary study.

Results

Table I lists the longest wavelength absorption bands for complexes of the nine donors with the π acceptors *p*-chloranil and TCNE in methylene chloride. Also listed are the HOMO coefficients calculated by the HMO method[7] using the following two sets of values for the empirical coulomb (α) and resonance (β) integrals: (i) $\alpha_O = \alpha_C + 2.0\beta_{C-C}$, $\beta_{C-O} = 0.8\beta_{C-C}$; (ii) $\alpha_O = \alpha_C + 2.0\beta_{C-C}$, $\beta_{C-O} = \beta_{C-C}$, where α_C and β_{C-C} are standard coulomb and resonance integrals for naphthalene. The first set are those from Streitwieser's table of suggested values[8] and are those used by Zweig[4] for the methoxybenzenes. The π system was taken to include the naphthalene ring system and a filled orbital on each oxygen; interaction between the π system and the ether methyl groups was not explicitly considered.

Plots of the frequencies (ν_{max}) of the charge-transfer bands *vs.* the second set of calculated HOMO coefficients (using $\beta_{C-O} = \beta_{C-C}$) are shown in Figures 1 and 2. The points show about the usual amount of scatter for correlations of this kind[4,6,9-11] with the 2,6-DMN point lying furthest from the best fit line in both cases.

Values of β_{C-C} calculated from the least-squares slopes in Figures 1 and 2 are 2.79 eV (std dev 0.33 eV) for TCNE and 2.77 eV (std dev 0.34 eV) for chloranil. Omission of the 2,6-DMN points does not significantly change the slopes ($\beta = 2.82 \pm 0.26$ and 2.80 ± 0.25 eV, respectively). Points in Figures 1 and 2 lie close to the plots for TCNE[10] and chloranil[12] complexes with aromatic hydrocarbons using HMO energies (slopes corresponding to $\beta = 3.06$ and 3.19 eV, respectively).

The more usual set of parameters, $\alpha_O = \alpha_C + 2.0\beta_{C-C}$ and $\beta_{C-O} = 0.8\beta_{C-C}$, leads to equally good linear correlations but with slopes corresponding to $\beta = 3.99$ eV (std dev 0.59 eV) (TCNE) and $\beta = 3.96$ eV (std dev 0.60 eV) (chloranil). These points thus deviate badly and systematically from the hydrocarbon correlations. It is interesting that although the correlation lines for the methoxybenzenes[4] and hydrocarbons[12] have similar slopes, those for the methoxybenzenes lie approximately 4×10^3 cm^{-1} below those for the hydrocarbons. Thus, use of $\beta_{C-O} = 0.8\beta_{C-C}$ seriously underestimates the donor strengths of the methoxyaromatics as measured by the positions of charge-transfer maxima. We

(7) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.
(8) See ref 7, p 135.
(9) M. J. S. Dewar and A. R. Lepley, *J. Amer. Chem. Soc.*, **83**, 4560 (1961).
(10) M. J. S. Dewar and H. R. Rogers, *ibid.*, **84**, 395 (1962).
(11) A. R. Lepley, *ibid.*, **84**, 3577 (1962).
(12) M. Naprš and R. Zahradnik, *Collect. Czech. Chem. Commun.*, **29**, 1545 (1964).

have therefore used the energies obtained using the second set of parameters to interpret the kinetic data (see below).

Use of the ω method[13] with $\alpha_O = \alpha_C + 2.0\beta_{C-C}$, $\beta_{C-O} = 0.8\beta_{C-C}$, and $\omega = 1.4$ leads to poorer correlations corresponding to $\beta = 4.22$ eV (std dev 0.80 eV) (TCNE) and $\beta = 4.19$ eV (std dev 0.80 eV) (chloranil).[14]

Table II lists observed first-order rate constants for acetolysis of TNF-OTs in the presence of the naphthyl ether donors. In no case was any deviation from strict first-order behavior detected over the range of the reaction followed (generally about 20–80% reaction). The assumed mechanism (above), together with the equilibrium condition for 1:1 complexation between reactant and donor, leads to eq 1,[15] where k_{obsd} is the

$$1/(k_{obsd} - k_u) = 1/(k_c - k_u) + 1/\{K[D]^0(k_c - k_u)\} \quad (1)$$

observed first-order rate constant in the presence of stoichiometric concentration of donor, $[D]_0$. Values of k_c and K obtained from the slope and intercept of plots of $1/(k_{obsd} - k_u)$ *vs.* $1/[D]_0$ (see Experimental Section) are listed in Table III. No such analysis was possible for 1,4-DMN since its low solubility, low rate of solution, and high catalytic activity restricted rate measurements to concentrations below about 0.02 M.

Formal activation parameters for acetolysis of TNF-OTs in the presence of 2,3-DMN varied from $\Delta H^{\pm} = 26.0 \pm 0.2$ kcal mol^{-1}, $\Delta S^{\pm}$ (85.3°) $= -10.8 \pm 0.4$ eu mol^{-1} in the absence of donor to $\Delta H^{\pm} = 21.6 \pm 0.2$ kcal mol^{-1}, $\Delta S^{\pm}$ (85.3°) $= -18.3 \pm 0.4$ eu mol^{-1} in the presence of 0.08 M (85.3°) 2,3-DMN. These trends are similar to those observed earlier with phenanthrene donor.[1b,15] Values of k_c at 64.78 and 85.30° lead to the following activation parameters for acetolysis of the TNF-OTs–2,3-DMN complex: $\Delta H^{\pm} = 25.3 \pm 2.7$ kcal mol^{-1}, $\Delta S^{\pm}$ (85.3°) $= -3.8 \pm 7.5$ eu mol^{-1}, again similar to earlier results with phenanthrene donor.

Discussion

The most striking observation in Table II is the tremendous catalytic effectiveness of the naphthyl ether donors. Thus, 0.0187 M 1,4-DMN increases the rate of acetolysis of TNF-OTs by a factor of 47.1! The 1:1 complexes investigated in this work vary from 26 times as reactive to 1900 times as reactive as uncomplexed reactant. As discussed previously,[2,1b] we view a complexed donor molecule as a loosely attached electron-supplying group. Some measure of the extent of this electron supply may be gained by comparing values of k_c in Table III with estimated rates of acetolysis of other substituted fluorenyl tosylates at 85.30°. TNF-OTs and the three related dinitro-9-fluorenyl tosylates (2,4, 2,5, and 2,7) have very similar enthalpies of activation for acetolysis.[16] Assuming a similar enthalpy of activation (24.9 kcal mol^{-1}) for 2-nitro-9-fluorenyl tosylate,[1b] its rate constant for acetolysis at 85.30° can be estimated to be about 4×10^{-3} sec^{-1} (maximum). Thus, a complexed 1,5-DMN, 1,7-DMN, or 1,6-DMN more than balances the effects of two (the 4 and the 7) nitro groups. By way of comparison, a complexed phenanthrene[15] has about the same effect as removal of the 2-nitro group.

TABLE II

RATES OF ACETOLYSIS OF 2,4,7-TRINITRO-9-FLUORENYL *p*-TOLUENESULFONATE[a] IN THE PRESENCE OF METHOXY- AND DIMETHOXYNAPHTHALENE DONORS

Donor	10^2[donor],[b] M	k,[c] sec^{-1}
	Temp = 85.30 ± 0.05°	
None	...	$4.56 \pm 0.03 \times 10^{-5}$
2-MN	5.63	$1.91 \pm 0.02 \times 10^{-5}$
	6.55	$2.01 \pm 0.02 \times 10^{-5}$
	7.49	$2.25 \pm 0.02 \times 10^{-5}$
	8.68	$2.54 \pm 0.03 \times 10^{-5}$
	9.36	$2.65 \pm 0.03 \times 10^{-5}$
1-MN	5.25	$7.12 \pm 0.07 \times 10^{-5}$
	6.23	$7.96 \pm 0.07 \times 10^{-5}$
	7.51	$9.37 \pm 0.09 \times 10^{-5}$
	8.46	$1.03 \pm 0.01 \times 10^{-4}$
	9.36	$1.12 \pm 0.01 \times 10^{-4}$
2,3-DMN	3.74	$2.67 \pm 0.03 \times 10^{-5}$
	5.59	$3.78 \pm 0.03 \times 10^{-5}$
	6.56	$4.22 \pm 0.04 \times 10^{-5}$
	7.49	$4.70 \pm 0.04 \times 10^{-5}$
	8.44	$5.22 \pm 0.04 \times 10^{-5}$
2,7-DMN	3.74	$4.50 \pm 0.04 \times 10^{-5}$
	4.44	$5.24 \pm 0.05 \times 10^{-5}$
	5.58	$6.21 \pm 0.05 \times 10^{-5}$
	6.93	$7.46 \pm 0.06 \times 10^{-5}$
	8.26	$8.59 \pm 0.07 \times 10^{-5}$
2,6-DMN	3.76	$4.64 \pm 0.04 \times 10^{-5}$
	4.25	$5.17 \pm 0.05 \times 10^{-5}$
	4.82	$5.55 \pm 0.04 \times 10^{-5}$
	6.10	$6.77 \pm 0.06 \times 10^{-5}$
	7.49	$8.07 \pm 0.07 \times 10^{-5}$
1,6-DMN	4.80	$2.06 \pm 0.02 \times 10^{-4}$
	5.62	$2.38 \pm 0.02 \times 10^{-4}$
	6.62	$2.77 \pm 0.02 \times 10^{-4}$
	7.47	$3.10 \pm 0.03 \times 10^{-4}$
	8.30	$3.44 \pm 0.03 \times 10^{-4}$
1,7-DMN	3.76	$1.23 \pm 0.01 \times 10^{-4}$
	4.86	$1.57 \pm 0.02 \times 10^{-4}$
	5.62	$1.83 \pm 0.02 \times 10^{-4}$
	7.51	$2.39 \pm 0.03 \times 10^{-4}$
	8.61	$2.73 \pm 0.02 \times 10^{-4}$
1,5-DMN	1.88	$1.65 \pm 0.02 \times 10^{-4}$
	2.34	$2.03 \pm 0.02 \times 10^{-4}$
	2.81	$2.43 \pm 0.03 \times 10^{-4}$
	3.23	$2.75 \pm 0.02 \times 10^{-4}$
1,4-DMN	1.87	$2.15 \pm 0.02 \times 10^{-4}$
	Temp = 64.78 ± 0.05°	
None	...	$4.68 \pm 0.03 \times 10^{-7}$
2,3-DMN	4.54	$4.65 \pm 0.05 \times 10^{-6}$
	5.76	$5.75 \pm 0.05 \times 10^{-6}$
	6.81	$6.69 \pm 0.06 \times 10^{-6}$
	7.68	$7.15 \pm 0.06 \times 10^{-6}$
	8.63	$7.94 \pm 0.05 \times 10^{-6}$

[a] Concentration of ester, 0.002 M. [b] Donor concentrations are corrected for solvent expansion and refer to the temperature of the kinetic measurements. [c] Listed with average deviations of 8–11 measurements.

The observed stabilities of the reactant–donor 1:1 complexes are difficult to interpret. Four of the donors for which complexation constants were determined (2,3-DMN, 2,7-DMN, 2,6-DMN, and 1,5-DMN) have twofold axes of symmetry while the 1:1 complex in every case has no element of symmetry. Therefore if one particular complex geometry is strongly favored over all others in all cases, or if free rotation exists within each complex (no preferred complex geometry),

(13) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949).
(14) A. L. McKenna, unpublished results.
(15) A. K. Colter, S. S. Wang, G. H. Megerle, and P. S. Ossip, *J. Amer. Chem. Soc.*, **86**, 3106 (1964).
(16) F. F. Guzik and A. K. Colter, *Can. J. Chem.*, **43**, 1441 (1965).

TABLE III

RESULTS OF ANALYSIS OF KINETIC DATA[a]

No.	Donor	Temp, °C	K, l. mol^{-1}	k_c, sec^{-1}	k_c/k_u
1	2-MN	85.30	2.28 ± 0.91	$1.2 \pm 0.5 \times 10^{-4}$	$2.6 \pm 1.1 \times 10$
2	1-MN	85.30	2.61 ± 0.25	$5.4 \pm 0.5 \times 10^{-4}$	$1.2 \pm 0.1 \times 10^{2}$
3	2,3-DMN	85.30	1.39 ± 0.22	$4.5 \pm 0.7 \times 10^{-4}$	$9.9 \pm 1.5 \times 10$
4	2,7-DMN	85.30	2.39 ± 0.19	$4.9 \pm 0.4 \times 10^{-4}$	$1.1 \pm 0.1 \times 10^{2}$
5	2,6-DMN	85.30	2.87 ± 0.42	$4.2 \pm 0.6 \times 10^{-4}$	$9.3 \pm 1.4 \times 10$
6	1,6-DMN	85.30	0.72 ± 0.11	$6.0 \pm 0.9 \times 10^{-3}$	$1.3 \pm 0.2 \times 10^{3}$
7	1,7-DMN	85.30	0.39 ± 0.10	$8.3 \pm 2.0 \times 10^{-3}$	$1.8 \pm 0.4 \times 10^{3}$
8	1,5-DMN	85.30	0.98 ± 0.22	$8.8 \pm 2.0 \times 10^{-3}$	$1.9 \pm 0.4 \times 10^{3}$
9	2,3-DMN	64.78	2.06 ± 0.36	$4.9 \pm 0.9 \times 10^{-5}$	$1.1 \pm 0.2 \times 10^{2}$

[a] Uncertainties in K and k_c taken as standard deviations obtained from weighted least-squares analysis.[15]

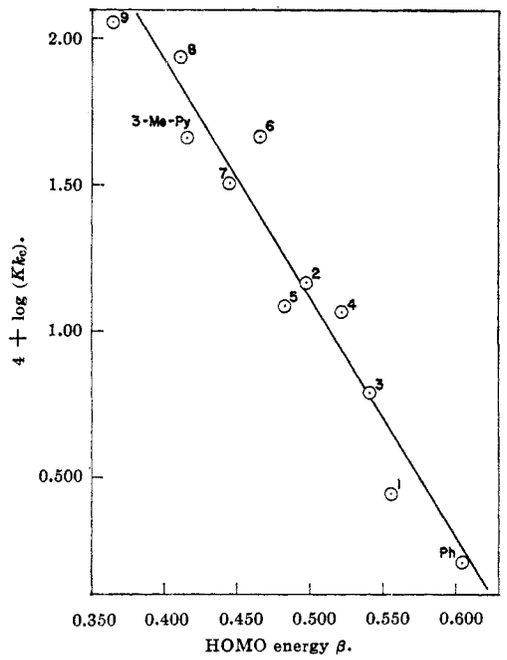


Figure 3.—Plot of log (Kk_c) *vs.* donor HOMO energy.

the complexation constants for the symmetrical donors will be twice those for the unsymmetrical donors, all other things equal. It is more likely, however, that a different number of acceptable complex geometries are available for each donor so that a simple statistical correction of this kind is unlikely to simplify the interpretation of the results.

The contribution of charge-transfer forces to the complex stability is expected to increase with increasing donor HOMO energy,[17] hence for a series of complexes involving a common acceptor and structurally related donors, a rough parallel between complexation constant and other experimental or theoretical measures of donor strength might be anticipated. Though a rough correlation between standard free energy of complexation and the energy of the corresponding charge-transfer absorption has been demonstrated in a number of cases,[18] a large amount of scatter is the rule. No such trend is evident in the present results, either with or without statistical corrections, and we are presently unable to understand the variations in K on the basis of any simple theoretical model. Among other factors which may be responsible for the differences in K observed here are differences in the preferred geometries of the complexes in solution and resulting differences in the degree to which intramolecular rotations within the donor and acceptor are frozen out in the complex.

The results summarized in Tables II and III reveal that the catalytic effectiveness of the methoxynaphthalene donors as measured by either the observed rate enhancement per M donor or by k_c/k_u qualitatively parallels the HOMO energies. Values of k_c/k_u fall into three groups: 2-MN, 26 ± 11; 1-MN and the three dimethoxynaphthalenes having two β-methoxy groups, 90–120; 1,6-DMN, 1,7-DMN, and 1,5-DMN, 1300–1900. Though no donor is seriously out of line with respect to its HOMO energy, experimental uncertainties in k_c and k_c/k_u are too large to make any distinction between members of the same group.

The nature of the analysis leading to k_c and K is such that overestimation of k_c results in underestimation of K and *vice versa*. Further, the product Kk_c is known with considerable accuracy in spite of large uncertainties in both k_c and K. Rearrangement of eq 1 leads to eq 2 for the observed rate constant in the presence of donor.

$$k_{obsd} = k_u + (k_c - k_u)K[D]_0/(1 + K[D]_0) \quad (2)$$

Thus it is evident that the initial slope of a plot of k_{obsd} *vs.* $[D]_0$ is equal, according to this analysis, to $(k_c - k_u)K \simeq Kk_c$. Values of Kk_c obtained in this way or from the data in Table III are known to ±5% or better.

The observed catalytic effect per M donor at low donor concentration, *i.e.*, Kk_c, shows a definite correlation with donor HOMO energy. Figure 3 shows a plot of log Kk_c *vs.* donor HOMO energy (set ii, Table I) with the least-squares straight line for the nine naphthyl ether points. Also included on this plot is phenanthrene[15] (Ph, $Kk_c = 1.63 \times 10^{-4}$, HOMO energy 0.605) and 3-methylpyrene[14] (3-Me-Py, $Kk_c = 45.8 \times 10^{-4}$, HOMO energy = 0.416[19]).

The first set of MO energies (Table I) leads to an equally good correlation of all points except that for 3-Me-Py. Again, based on the limited data at hand, use of the second set of parameters (above) appears to provide a measure of donor strength for the methoxynaphthalenes which is more consistent with that obtained for hydrocarbon donors from HMO calculations. However, this choice is arbitrary[7] and for the moment must be considered highly tentative being based, for the kinetic data, on a single point. As more data become available it may turn out that different sets of param-

(17) R. S. Mulliken, *J. Amer. Chem. Soc.*, **74**, 811 (1952).

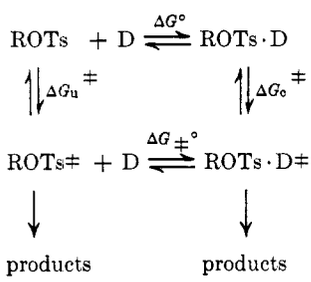
(18) G. Briegleb, "Electronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961, p 130 ff.

(19) The effect of the 3-methyl group on the HOMO energy of pyrene was approximated by first-order perturbation theory, following A. R. Lepley [*J. Amer. Chem. Soc.*, **86**, 2545 (1964)] using a value of −0.21 for the inductive perturbation parameter, h.

eters are most appropriate for correlation of spectral and kinetic data.

The significance of the two measures of catalytic effectiveness can be shown by rewriting the proposed mechanism to include equilibrium between initial and transition states[20] as shown in Scheme I. The symbols

SCHEME I



ROTs‡ and ROTs·D‡ represent uncomplexed and complexed transition states, respectively. The four standard free energy changes in the above scheme are related by eq 3. We may now choose to examine

$$\Delta G^0 + \Delta G_c^{\ddagger} = \Delta G_{\ddagger}^{\ 0} + \Delta G_u^{\ddagger} \quad (3)$$

either k_c/k_u or Kk_c as a measure of catalytic effectiveness. From eq 4 it is apparent that an increase in k_c or k_c/k_u reflects an increase in the *difference* between the standard free energies of complexation for the reactant and uncomplexed transition state. It is possible that steric factors influencing complex stability may have some tendency to cancel in examining the difference $\Delta G_{\ddagger}^{\circ} - \Delta G^{\circ}$. However, the preferred complex geometry for a given donor is not necessarily the same for the initial and transition states and steric effects therefore do not necessarily cancel. The quantity Kk_c, in contrast, reflects only the stability of the transition state 1:1 complex, hence we should normally expect the same lack of success in correlating this quantity with MO theory as ground-state complex stabilities (see above). The moderately successful correlation observed here is likely due in part to the fact that the total spread in ΔG values is much larger than in previous correlations[18] of this kind.

$$-RT \ln (k_c/k_u) = \Delta G_c^{\ddagger} - \Delta G_u^{\ddagger} = \Delta G_{\ddagger}^{\ 0} - \Delta G^0 \quad (4)$$

$$-RT \ln Kk_c = \Delta G^0 + \Delta G_c^{\ddagger} - RT \ln (kT/h) = \Delta G^0 + \Delta G_c^{\ddagger} + \text{constant} = \Delta G_{\ddagger}^{\ 0} + \Delta G_u^{\ddagger} + \text{constant} = \Delta G_{\ddagger}^{\ 0} + \text{constant} \quad (5)$$

The electronic contribution to the complex stability is not expected on theoretical grounds to be linear in the donor HOMO energy; rather it approaches zero asymptotically as the difference between the energy of the lowest vacant molecular orbital (LVMO) of the acceptor and the donor HOMO energy increases.[21] However, the relationship is predicted to be close to linear over a moderate range in HOMO energies if the acceptor LVMO and donor HOMO energies are sufficiently different.

Considerably more data will be necessary to decide whether k_c or Kk_c is the more closely related to the donor HOMO energy. At present experimental uncertainties in k_c are too large to allow any decision on this point. Nevertheless a correlation between catalytic effectiveness (whichever measure is used) and donor HOMO energy does exist and we consider this to be strong evidence for the proposal[2] that the catalysis involves charge-transfer complexing. The fact that the two hydrocarbon donors (Figure 3) do not seem to be out of line suggests that direct nucleophilic participation is not involved in catalysis by the naphthyl ether donors; however, the evidence is not strong on this point.

Experimental Section[22]

Materials.—Spectral grade methylene chloride was employed without further purification in all spectral studies. Chloranil, Fisher reagent grade, was sublimed once before using, mp 290–291.5° (sealed tube). Tetracyanoethylene, Eastman Kodak White Label, was crystallized twice from chlorobenzene anp sublimed twice at 125° to obtain white crystals, mp 199–201°. 1-Methoxynaphthalene, Eastman Kodak White Label, was redistilled once before using, bp 165–166 (20 mm). 2-Methoxynaphthalene was prepared from 2-naphthol (Fisher Certified reagent) by a procedure similar to that of Naylor and Gardner.[23] The solid product was washed with aqueous base and water, dried, and crystallized from 95% ethanol, mp 72–74° (lit.[24] mp 72.5–73.0°). 2,3-Dimethoxynaphthalene was prepared by alkaline methylation of 2,3-dihydroxynaphthalene (Aldrich research grade) following the procedure used for 2-methoxynaphthalene, mp 116–117.5° (lit.[25] mp 116.5°). 2,6-Dimethoxynaphthalene, Baker reagent grade, was washed twice with aqueous sodium hydroxide and crystallized from 95% ethanol, mp 152–154° (lit.[26] mp 150°). 2,7-Dimethoxynaphthalene was prepared by alkaline methylation of 2,7-dihydroxynaphthalene (Aldrich research grade) following the procedure used for 2-methoxynaphthalene, melting point after crystallization from 95% ethanol 137–138.5° (lit.[27] mp 138°). 1,6-Dimethoxynaphthalene was prepared by alkaline methylation of purified 1,6-dihydroxynaphthalene by the procedure used for 2-methoxynaphthalene, mp 58–59.5° (lit.[28] mp 60–61°). 1,6-Dihydroxynaphthalene, Columbia technical grade, was purified by repeated crystallization from benzene and charcoal decolorization until it had mp 137–139°. 1,7-Dimethoxynaphthalene, Aldrich research grade, was purified by distillation, bp 150–152° (12 mm). 1,5-Dimethoxynaphthalene was prepared by alkaline methylation of purified 1,5-dihydroxynaphthalene in the usual way, mp 181–183° (lit.[29] mp 183–184°). 1,5-Dihydroxynaphthalene, Baker technical grade, was purified using the procedure described by Wheeler.[30] 1,4-Dimethoxynaphthalene was prepared from 1,4-dihydroxynapthalene (Eastman Kodak practical grade) by the same alkaline methylation procedure except under nitrogen atmosphere. After crystallization from petroleum ether (bp 65–110°) the product had mp 83.5–85° (lit.[31] mp 86–87.5°). Infrared examination of the methoxy- and dimethoxynaphthalenes did not indicate any contamination by unreacted phenolic materials. The purity of 1,6-, 2,6-, and 1,5-dimethoxynaphthalene was further confirmed by vapor phase chromatography. 2,4,7-Trinitro-9-fluorenyl *p*-toluenesulfonate, mp 208–210°, was prepared as previously described.[32]

Charge-Transfer Spectra.—All spectral measurements were made at 20° in 1-cm cells in the range of 300–797 mμ on a Cary Model 11 spectrophotometer. Solutions were prepared by mixing equal volumes of 0.02 *M* donor and acceptor solutions in methylene chloride. Charge-transfer maxima estimated from the

(20) J. L. Kurz, *J. Amer. Chem. Soc.*, **85**, 987 (1963).

(21) This is most readily seen using the LCMO model of R. L. Flurry, *J. Phys. Chem.*, **69**, 1927 (1965), but follows from the Mulliken treatment as well.

(22) Melting points and boiling points are uncorrected.

(23) C. A. Naylor and J. H. Gardner, *J. Amer. Chem. Soc.*, **53**, 4109 (1931).

(24) V. H. Dermer and O. C. Dermer, *J. Org. Chem.*, **3**, 289 (1938).

(25) H. Kauffmann and A. Beisswenger, *Ber.*, **36**, 561 (1903).

(26) R. Willstätter and J. Parnas, *ibid.*, **40**, 1406 (1907).

(27) O. Fischer and W. Kern, *J. Prakt. Chem.*, [2] **94**, 34 (1916).

(28) O. Fischer and C. Bauer, *ibid.*, [2] **94**, 1 (1916).

(29) W. H. Bentley, R. Robinson, and C. Weizmann, *J. Chem. Soc.*, **91**, 104 (1997).

(30) A. S. Wheeler and D. R. Ergle, *J. Amer. Chem. Soc.*, **52**, 4872 (1930).

(31) B. R. Baker and G. H. Coleman, *ibid.*, **64**, 2657 (1942).

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

spectrometer traces are estimated to be reliable to ±5 mμ for the TCNE spectra and to ±10–15 mμ for the broader chloranil maxima. In cases where two bands seriously overlapped, the observed maxima were corrected following the procedure described by Voigt and Reid.[33] The corrections varied from 3 to 7 mμ (Table I) and do not significantly affect the MO correlations.

Kinetic Measurements.—The kinetic procedures have been described previously[15] as has the analysis of the data to obtain the quantities k_c and K. Standard deviations reported in Table III are those obtained using the weighed least-squares procedure described by Parratt.[34]

(33) E. M. Voigt and C. Reid, *J. Amer. Chem. Soc.*, **86**, 3931 (1964).

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

Registry No.—**1**, 93-04-9; **2**, 2216-69-5; **3**, 10103-06-7; **4**, 3469-26-9; **5**, 5486-55-5; **6**, 3900-49-0; **7**, 5309-18-2; **8**, 10075-63-5; **9**, 10075-62-4; 2,4,7-trinitro-9-fluorenyl *p*-toluenesulfonate, 6673-16-1.

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Mechanisms of Reactions of Thiolsulfinates (Sulfenic Anhydrides). II. The Thiolsulfinate–Mercaptan Reaction[1]

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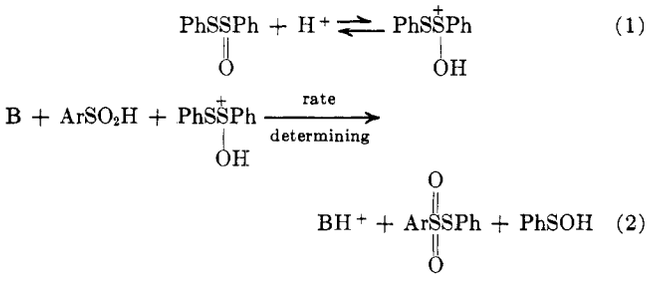
In acetic acid–1% water in the presence of some sulfuric acid phenyl benzenethiolsulfinate (I) reacts readily with alkanethiols to yield phenyl alkyl disulfides. Kinetic study of the reaction shows that it is first order in both mercaptan and thiolsulfinate and subject to specific H^+ catalysis. A mechanism (Chart II) is proposed which involves nucleophilic attack of the mercaptan on the sulfenyl sulfur of sulfinyl-protonated I. This mechanism differs from that for the related reaction of I with aryl sulfinic acids (eq 1 and 2) in that transfer of the proton of the thiol to a general base is *not* concerted with the formation of the new S–S bond. This finding confirms the probable correctness of an explanation advanced earlier[2] for the need for such a proton transfer in the rate-determining step of the sulfinic acid reaction. The I–mercaptan reaction can be catalyzed by the addition of small amounts of alkyl sulfides. Study of the kinetics of the sulfide-catalyzed reaction shows that it involves the same rate-determining step (eq 3) as was previously suggested[2] for sulfide catalysis of the thiolsulfinate–sulfinic acid reaction and thereby demonstrates rather unequivocally the correctness of the mechanism which has been proposed[2] for the sulfide-catalyzed I–$ArSO_2H$ reaction.

In moist acetic acid containing some sulfuric acid phenyl benzenethiolsulfinate (I), PhS(O)SPh, reacts quite readily with aryl sulfinic acids ($ArSO_2H$) to produce as the almost exclusive product the phenyl arenethiolsulfonate, $ArSO_2SPh$.[2] Kinetic studies have shown that this thiolsulfinate–sulfinic acid reaction is first order in both thiolsulfinate and sulfinic acid and that it is also apparently general acid catalyzed. On the basis of this and other evidence a mechanism involving a rate-determining general base catalyzed attack of the sulfinic acid on the protonated thiolsulfinate (eq 2) was proposed.[2] It was also suggested

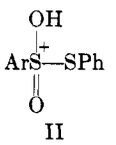


(1) This research supported by the National Science Foundation, Grant GP-6952.

(2) J. L. Kice, C. G. Venier, and L. Heasley, *J. Amer. Chem. Soc.*, **89**, 3557 (1967).

(3) S. K. Hall and E. A. Robinson, *Can. J. Chem.*, **42**, 1113 (1964), have shown that the pK_a of the conjugate acid of dimethyl sulfone is −12.3.

that the reason nucleophilic attack of the sulfinic acid on protonated I should require general base catalysis is because sulfone groups are such extremely weak basic sites[3] that II, which would result from a normal nucleophilic displacement by $ArSO_2H$, would be an extremely unstable intermediate formed only with great difficulty. By making transfer of the proton from $ArSO_2H$



II

concerted with the formation of the new S–S bond the need to go through II as an intermediate is avoided. However, since this is achieved only at the expense of an increase in the molecularity of the reaction, one might expect that similar displacements involving species NuH, where the intermediate HNu^+–SPh was not as energetically unfavorable as II, would not require the presence of the general base in the rate-determining step and would therefore exhibit specific oxonium ion rather than general acid catalysis.

Another important feature of the thiolsulfinate–sulfinic acid reaction is that the reaction can be dramatically catalyzed by the addition of small amounts of alkyl sulfides.[2] The sulfide-catalyzed process is first order in both thiolsulfinate and alkyl sulfide, but its rate is independent of sulfinic acid concentration. It exhibits specific H^+ catalysis, and the variation of its rate with sulfide structure indicates that the sulfide acts as a nucleophile. The mechanism shown in Chart I was accordingly suggested for the sulfide-catalyzed reaction. It involves rate-determining nucleophilic attack by R_2S on the protonated thiolsulfinate (eq 3). The species R_2S^+–SPh (III) so formed then