Steric Effects. III.
Bimolecular Nucleophilic Substitution

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Abstract: Rate data for 18 sets of bimolecular nucleophilic substitution involving compounds of the type XCH_2Y, where X = H or alkyl, and Y is a leaving group, were correlated with the equation, $\log k_X = \alpha\sigma_{IX} + \beta\sigma_{RX} + \psi\upsilon_X + h$, and $\log k_X = \psi\upsilon_X + h$. The results of the correlations show that the effect of the X group is predominantly if not entirely steric. As the υ constants were defined from the esterification of carboxylic acids and represent a steric effect on the formation of an approximately sp^3 hybridized transition state, they probably do not provide the best representation of the steric effect in bimolecular nucleophilic substitution where the X group exerts a steric effect upon an approximately sp^2 hybridized transition state. New steric effect substituent constants, υ', were therefore defined from the rate constants for the reaction of XCH_2Br with Br^- in MeAc at 25°. Values of υ' for eight alkyl groups are given. The magnitude of the steric effect in bimolecular nucleophilic substitution is greater than the magnitude of the steric effect in esterification and acid hydrolysis of esters, or in basic hydrolysis of esters. Values of υ' are smaller than values of υ for most groups, however.

Consider the set of compounds XCH_2Y in which X is an alkyl group or hydrogen atom, and Y is a leaving group. It has been stated that the effect of the X group on the rate of bimolecular nucleophilic substitution includes both steric and polar increments.[1] Okamoto, Nitta, Imoto, and Shingu[2] have reported that the Taft[3] σ^* and E_S values cannot be applied to bimolecular substitution reactions of X^1X^2CHY. We have examined the application of the modified Taft equation[4] (eq 1) to this problem. Okamoto et al.[2] have reexamined the equation (eq 2) first proposed by Hine[5] and

$$\log k_X = \psi\upsilon_X + h \qquad (1)$$

$$\log (k/k^\circ) = rA \qquad (2)$$

Taft.[6] In this equation, r is a reaction constant, and A is a structural parameter, $\log k$ and $\log k^\circ$ are rate constants for bimolecular nucleophilic substitution of the substituted compound and of EtY, respectively. The A values were estimated as arithmetic means of the $\log k$ values for 35 sets of bimolecular substitution reactions studied. We have examined the correlation of these A values for compounds of the type XCH_2Y with eq 3. This equation includes both terms

$$A = \alpha\sigma_{IX} + \beta\sigma_{RX} + \psi\upsilon_X + h \qquad (3)$$

characteristic of the electrical effect (σ_I,σ_R) and a steric parameter (υ).

The A values used in this correlation are given in Table I. The results of the correlation are reported in Table II. Examination of the "Student t" tests for the significance of the coefficients α, β, and ψ shows that only ψ is significant. The A values were therefore correlated with eq 4. The results of

$$A = \psi\upsilon_X + h \qquad (4)$$

this correlation are given in Table III. This correlation was significant at the 99.5% confidence level (CL). The success of this correlation encouraged us to investigate the correla-

Table I. Data used in Correlations

1	A constants for XCH_2[a] H, 1.308; Me, 0.000; Et, −0.359; Pr, −0.371; *i*-Pr, −1.387; *t*-Bu, −4.875
2	10^5k_2, XCH_2Br + LiCl in MeAc at 25°[b] H, 600; Me, 9.88; Et, 6.45; *i*-Pr, 1.53; *t*-Bu, 0.00026
3	10^5k_2, XCH_2Br + LiBr in MeAc at 25°[c] H, 13,000; Me, 170; Et, 110; *i*-Pr, 5.7; *t*-Bu, 0.00026
4	10^5k_2, XCH_2Br + LiI in MeAc at 25°[d] H, 25,000; Me, 166; Et, 137; *i*-Pr, 6.0; *t*-Bu, 0.0020
5	10^5k_2, XCH_2I + LiCl in MeAc at 25°[e] H, 468; Me, 42.0; Et, 24.6; *i*-Pr, 1.62; *t*-Bu, 0.00058
6	10^5k_2, XCH_2I + LiBr in MeAc at 25°[f] H, 27,000; Me, 1400; Et, 1050; *i*-Pr, 32
7	10^3k_2, $XCH_2I + I^-$ in EtOH at 50°[g] Me, 3.20; Et, 2.35 (55°); Pr, 1.09; *i*-Pr, 0.150; Bu, 1.36; *i*-PrCH$_2$, 0.572
8	10^3k_2, XCH_2Br + NaOE*t*, in EtOH at 55°[h,i] H, 34.4; Me, 1.95; Et, 0.547; *i*-Pr, 0.058; *t*-Bu, 8.26×10^{-6}; Pr, 0.396; Bu, 0.357
9	10^3k_2, XCH_2Br + NaOEt, in EtOH at 95°[h] H, 965; Me, 64.7; *i*-Pr, 2.62; *t*-Bu, 6.49×10^{-4}
10	10^5k_2, $XCH_2Br + SCN^-$ in EtOH at 25.00°[j] Me, 1.67; Et, 1.15; Pr, 1.14; Bu, 1.20; BuCH$_2$, 1.22; BuCH$_2$CH$_2$, 1.24; Bu(CH$_2$)$_3$, 1.27; *i*-Pr, 0.05; *i*-PrCH$_2$, 0.73
11	k, XCH_2I + sodium eugenoxide in EtOH at 57.5°[k] H, 3.00 (55°); Me, 1.00; Et, 0.38; Pr, 0.35; Bu, 0.33; *i*-Pr, 0.136; *i*-PrCH$_2$, 0.203
12	k, XCH_2I + sodium eugenoxide in EtOH at 68°[k] Me, 2.50; Et, 1.04; Pr, 0.94; Bu, 0.87; *i*-Pr, 0.34; *i*-PrCH$_2$, 0.51
13	10^4k_2, $XCH_2Br + Na_2S_2O_3$ in 50% EtOH−H_2O at 12.5°[l] H, 285; Me, 2.43; Et, 1.266; *i*-Pr, 0.0459
14	10^5k_2, $XCH_2I + Bu_3P$ in MeAc at 34.97°[m] H, 26,000; Me, 154; Et, 63.7; Pr, 56.8; *i*-Pr, 4.94
15	10^4k_2, XCH_2Br + NaOMe in MeOH at 80.0°[a] H, 814; Me, 90.6; Et, 33.5; Pr, 33.4; *i*-Pr, 6.75
16	10^4k_2, XCH_2Br + NaOPh in MeOH at 80°[a] H, 284; Me, 62.1; Et, 28.9; Pr, 30.8; *i*-Pr, 5.12
17	10^6k_2, $XCH_2Br + PhNMe_2$ in MeOH at 80°[a] H, 27.8; Me, 178; Et, 86.7; Pr, 90.3; *i*-Pr, 3.10
18	10^6k_2, XCH_2Br + pyridine in MeOH at 80°[a] H, 27.1; Me, 152; Et, 84.2; *i*-Pr, 2.54
19	10^5k_1, XCH_2OTs + AcOH in AcOH at 70°[n] H, 0.0516;; Me, 0.0442; *i*-Pr, 0.0179; *t*-Bu, 0.00417; Et, 0.0355; *n*-C$_6$H$_{13}$, 0.0355; *n*-C$_7$H$_{15}$, 0.0355

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Table II. Results of Correlation with Equation 3 and 5

Set	α	β	ψ	h	R^a	F^b	$r_{12}{}^c$	$r_{13}{}^c$	$r_{23}{}^c$	$s_{\mathrm{est}}{}^d$	$s_\alpha{}^d$	$s_\beta{}^d$	$s_\psi{}^d$	$s_h{}^d$	n^e
1A	19.8	−26.6	−6.67	1.47	0.984	20.99^k	0.840	0.827	0.846	0.587	22.0^c	11.6^n	1.34^k	0.574^n	6
2A	20.8	−22.5	−6.30	2.83	0.997	48.87^m	0.863	0.853	0.846	0.386	16.2^o	7.82^o	0.907^l	0.382^l	5
3A	−19.6	−16.0	−7.08	4.16	0.998	85.77^l	0.863	0.853	0.846	0.309	13.0^q	6.27^o	0.727^l	0.306^k	5
4A	0.695	−14.8	−7.21	4.45	0.997	65.13^l	0.863	0.853	0.846	0.373	15.7^q	7.57^o	0.878^l	0.370^l	5
5A	1.32	−24.9	−7.28	2.73	0.996	39.93^m	0.863	0.853	0.846	0.415	17.4^q	8.41^o	0.976^l	0.411^l	5
7A	−46.2	27.9	−1.63	2.51	0.954	3.376^m	0.593	0.754	0.717	0.297	25.4^o	15.2^o	1.57^o	2.78^p	5
8A	20.9	−30.8	−7.39	5.66	0.991	52.71^g	0.827^l	0.827^l	0.837^l	0.400	14.7^o	7.40^k	0.905^h	0.390^f	7
11A	−9.33	4.93	−1.12	0.469	0.934	6.874^l	0.857^l	0.531	0.763	0.228	11.4^o	5.96^o	0.511^n	0.226^n	7
12A	−13.2	4.18	−0.923	0.522	0.837	1.558^m	0.281	0.797	0.498	0.257	19.9^p	10.2^p	1.32^p	2.26^q	6
14A	−4.66	3.91	−4.13	4.45	0.982	9.242^m	0.855	0.679	0.935	0.511	31.9^q	27.0^q	3.21^o	0.511^l	5
15A	−2.49	−3.61	−3.14	2.94	0.964	4.435^m	0.855	0.679	0.935	0.404	25.2^q	21.3^q	2.54^o	0.404^l	5
16A	−9.43	1.03	−2.21	2.48	0.932	2.203^m	0.855	0.679	0.935	0.457	28.5^p	24.1^q	2.87^p	0.456^n	5
17A	−44.9	12.2	−0.496	1.50	0.743	0.410^m	0.855	0.679	0.935	0.927	57.8^p	48.8^q	5.81^q	0.925^o	5
19A	1.52	−7.64	−1.58	−1.28	0.963	12.83^k	0.829^l	0.843^l	0.845^l	0.144	5.51^q	2.63^l	0.337^i	0.142^h	7

Confidence levels of F and of "Student t" tests on s_α, s_β, s_ψ, s_h are given as superscripts. [a] Multiple correlation coefficient. [b] F test for significance of regression. [c] Partial correlation coefficient of σ_I on σ_R, σ_I on ν, σ_R on ν. [d] Standard errors of the estimate, α, β, ψ, and h. [e] Number of points in set. [f] 99.9% confidence level (CL). [g] 99.5% CL. [h] 99.0% CL. [i] 98.0% CL. [j] 97.5% CL. [k] 95.0% CL. [l] 90.0% CL. [m] <90.0% CL. [n] 80.0% CL. [o] 50.0% CL. [p] 20.0% CL. [q] <20.0% CL.

Table III.

Set	ψ	h	r^a	F^b	$s_{\mathrm{est}}{}^c$	$s_\psi{}^c$	$s_h{}^c$	n^d
1B	−4.96	2.16	0.942	31.52^f	0.792	0.883^g	0.641^j	6
2B	−5.07	3.36	0.968	44.48^g	0.680	0.760^g	0.558^g	5
3B	−5.45	4.67	0.981	75.65^f	0.561	0.626^g	0.460^g	5
4B	−5.75	4.91	0.985	98.05^f	0.529	0.590^g	0.434^g	5
5B	−4.82	3.50	0.947	26.04^i	0.846	0.945^h	0.694^h	5
6B	−3.47	4.63	0.939	14.90^k	0.505	0.899^k	0.485^h	4
7B	−1.80	1.23	0.609	1.772^l	0.454	0.135^n	1.00^n	5
8B	−5.28	6.55	0.934	34.34^f	0.809	0.900^g	0.648^e	7
9B	−4.97	5.64	0.958	22.56^j	0.936	1.05^j	0.809^h	4
10B	−1.18	0.748	0.331	0.863^l	0.471	1.27^n	0.907^n	9
11B	−1.37	0.468	0.917	26.55^f	0.197	0.265^g	0.175^j	7
12B	−1.38	0.895	0.765	5.654^k	0.214	0.582^k	0.415^k	6
13B	−4.75	2.59	0.985	64.74^i	0.331	0.590^h	0.318^h	4
14B	−4.53	4.45	0.982	81.25^f	0.299	0.502^g	0.286^e	5
15B	−2.46	2.99	0.956	31.74^i	0.259	0.436^h	0.249^g	5
16B	−1.93	2.55	0.910	14.46^j	0.302	0.507^j	0.289^g	5
17B	−0.320	1.78	0.138	0.058^l	0.792	1.33^p	0.758^m	5
18B	−0.680	1.80	0.281	0.171^l	0.926	1.64^o	0.886^m	4
19B	−0.854	−1.03	0.837	11.69^i	0.226	0.250^h	0.183^g	7

Confidence levels of F and of "Student t" tests of s_ψ and s_h are indicated by superscripts. [a] Correlation coefficient. [b] F test for significance of regression. [c] Standard errors of est, ψ, and h. [d] Number of points in set. [e] 99.9% confidence level (CL). [f] 99.5% CL. [g] 99.0% CL. [h] 98.0% CL. [i] 97.5% CL. [j] 95.0% CL. [k] 90.0% CL. [l] <90.0% CL. [m] 80.0% CL. [n] 50.0% CL. [o] 20.0% CL. [p] <20.0% CL.

tion of rate data for bimolecular nucleophilic substitution with eq 5 and with eq 1. Equation 5 is intended to detect the

$$\log k_X = \alpha\sigma_{IX} + \beta\sigma_{RX} + \psi\upsilon_X + h \qquad (5)$$

presence or absence of electrical effects of the substituents. A significant electrical effect will be shown by a confidence level of the "Student t" test of α and/or β of 90.0% or better, coupled with a confidence level for the F test for the significance of the correlation of 90.0% or better. It is also necessary for the partial correlation coefficients r_{13} and r_{23} to have confidence levels less than 90.0%.

The data used are set forth in Table I. Results of correlations with eq 5 and 1 are given in Tables II and III, respectively. The σ_I constants are taken from our compilation;[7] the σ_R constants are obtained from eq 6 using the σ_p con-

$$\sigma_R = \sigma_p - \sigma_I \qquad (6)$$

stants taken from the collection of McDaniel and Brown.[8] The υ constants are from our first publication in this series.[4]

Results

Of the 14 sets correlated with eq 5, only five gave significant correlations. One gave excellent, one gave fair, and three gave poor correlation. Of these sets, two showed significant partial correlation coefficients r_{13} and r_{23}. Thus, only the remaining three sets may be used to give an indication of the importance of electrical effects. In all three of these sets, the "Student t" tests of α and β showed confidence levels less than 80.0%. These results in combination with the result obtained for the correlation of the A values of eq 2 with eq 3 (set 1A) lead to the conclusion that, in compounds of the type XCH_2Y, electrical effects are either unimportant or constant.

Of the 18 sets of data correlated with eq 1, five gave excellent, one gave very good, four gave good, two gave fair, and two gave poor results. Four sets did not give significant correlation. Thus, most of the sets studied gave significant correlation with eq 1.

Discussion

Our results suggest that the effect of an alkyl group upon the rate of bimolecular nucleophilic substitution in the sets XCH_2Y is predominantly steric. This conclusion is based on the following arguments. (1) Those sets which gave significant correlations with eq 5 and did not have significant values of the partial correlation coefficients do not have significant values of α and β. Then we can conclude that electrical effects are unimportant. (2) The υ values were derived in the first paper of this series from correlations of rates of esterification and acid catalyzed ester hydrolysis with primary υ values defined from eq 7, where r_{VX} and r_{VH} are the

Table IV. Values of υ and υ'

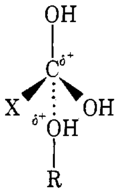
X	υ^a	υ'	Set^b	X	υ^a	υ'	Set^b
H	0	0	3	*i*-Pr	0.76	0.62	3
Me	0.52	0.35	3	*t*-Bu	1.24	1.23	3
Et	0.56	0.38	3	Pr	0.68	0.42	8
i-PrCH$_2$	0.98	0.55	11	Bu	0.68	0.42	8

[a] From ref 4. [b] Set from which υ' values were obtained.

$$\upsilon_X = r_{VX} - r_{VH} = r_{VX} - 1.20 \qquad (7)$$

Van der Waals radii for X and H, respectively. The correlations obtained for the rate constants with the primary values show that the effect of substituents is purely steric. As 14 of the 18 sets correlated with eq 1 gave significant results, we are forced to the conclusion that only steric effects are operative. (3) In the second paper of this series,[9] we have shown that, in the basic hydrolysis of esters, alkyl substituents on the acyl moiety exhibit only steric effects. This is the case even though the reaction is known to be susceptible to polar effects.

The success of the correlations with eq 1 is particularly remarkable in view of the fact that the υ constants are defined from the rates of esterification of carboxylic acids. The transition state for esterification of XCO_2H with the alcohol ROH is I, in which the carbon atom undergoing attack is hydridized approximately sp^3. By contrast, the transition state for bimolecular nucleophilic substitution of XCH_2Y by the nucleophile Nu^- is II, in which the carbon atom undergoing attack is approximately sp^2 hybridized. The marked difference between transition states I and II implies that the υ constants defined from I represent only an approximation of the steric effect of X in transition state II. Ideally, we should prefer to define a set of steric parameters, υ', from an appropriate set of rate constants for bimolecular nucleophilic substitution of XCH_2Y. For this purpose, we have chosen as our reference reaction the reaction of bromide ion with XCH_2Br in acetone at 25° (set 3, Table I). As our reference substituent, we again choose hydrogen which we assume has no steric effect, thus, υ'_H = 0.00. To place the υ' values on the same scale as the υ values, we have chosen for ψ' the value obtained from the correlation of set 3 with eq 1, −5.45. Having defined υ'_H and ψ', we may now calculate values of υ' for various alkyl groups. The values obtained are shown in Table IV together with the corresponding υ values for the purpose of comparison. Values of υ' for other groups are obtained from correlations with eq 8. Results of correlations with eq 8 are shown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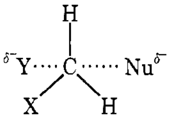
II

$$\log k_X = \psi'\upsilon' + h' \qquad (8)$$

in Table V. Of 18 sets correlated with eq 8, 11 gave excellent, 3 gave very good, and 2 gave good results. Two sets did not give significant correlation. The υ' values provide us with an opportunity to distinguish between steric effects resembling those in transition state I, which are best correlated by the υ constants and steric effects resembling those in transition state II, which are best correlated by the υ' constants. We hope to apply this technique to other sets of data.[10]

The values of ψ' obtained suggest that the magnitude of the steric effect in bimolecular nucleophilic substitution is generally greater than the magnitude of the steric effect in esterification and acid hydrolysis of esters, or in basic hydrolysis of esters.[4,9] The sign of ψ' shows steric retardation.

The data available do not permit any conclusions to be drawn concerning the variation of ψ' with solvent, nucleophile, leaving group, or temperature. It is interesting to note that, although the magnitude of the steric effect as measured by the ψ' values (or for that matter, the ψ values) is greater for bimolecular nucleophilic substitution that for ester hydrolysis, the υ constants defined from the latter reaction are usually larger than those defined from the former reaction. In fact, comparison of transition states I and II suggests that there is more hindrance in I than in II.

All of the sets studied above are of the type XCH_2Y. For many of these sets, values of the rate constant for the compound Me_2CHY have been reported. A number of authors have handled the problem of steric effects due to multiple substitution by eq 9, where E_S is the Taft steric parameter.[3]

$$\log k_{X^1X^2} = \delta\Sigma E_S + \log k^\circ \qquad (9)$$

Then for the A values we may write

$$A = \psi'\Sigma\upsilon' + h' \qquad (10)$$

From the correlation of A values with eq 8 (set 1C, Table V), we obtain values of ψ' and h which, when substituted in eq 10 together with the appropriate A value, give an observed value of $\Sigma\upsilon'$ of 0.63 which is in fair agreement with

Table V

Set	ψ'	h'	r^a	F^b	$s_{est}{}^c$	$s_{\psi'}{}^c$	$s_{h'}{}^c$	n^d
1C	−5.12	1.61	0.995	400.9^e	0.235	0.256^e	0.160^e	6
2C	−5.10	2.87	0.993	222.8^e	0.312	0.342^e	0.225^g	5
4C	−5.73	4.32	0.9997	5162^e	0.0728	0.0798^e	0.0525^e	5
5C	−4.95	3.09	0.991	164.8^f	0.352	0.386^g	0.254^g	5
6C	−4.61	4.59	0.983	55.96^i	0.273	0.616^h	0.249^g	4
7C	−4.44	2.03	0.975	75.70^e	0.120	0.511^e	0.238^g	6
8C	−5.48	4.88	0.993	209.7^e	0.345	0.378^e	0.249^e	5
9C	−5.11	3.32	0.993	136.2^g	0.394	0.438^g	0.311^g	4
10C	−4.67	1.97	0.869	12.33^i	0.313	1.33^j	0.621^j	6
11C	−2.21	0.516	0.961	47.73^f	0.145	0.320^g	0.131^h	6
12C	−2.61	1.12	0.929	25.07^g	0.123	0.521^g	0.243^h	6
13C	−6.12	2.47	0.9996	2686^e	0.0522	0.118^e	0.476^e	4
14C	−6.07	4.33	0.995	311.1^e	0.155	0.345^e	0.140^e	5
15C	−3.37	2.94	0.988	118.0^f	0.139	0.310^g	0.126^e	5
16C	−2.74	2.55	0.974	56.13^f	0.164	0.366^g	0.149^e	5
17C	−1.04	1.99	0.338	0.388^l	0.752	1.68^o	0.682^k	5
18C	−1.33	1.93	0.433	0.460^l	0.867	1.96^o	0.791^m	4
19C	−0.954	−1.15	0.973	53.22^g	0.119	0.131^g	0.0860^e	5

See corresponding footnotes to Table III.

the value of 0.70 calculated from υ' for the methyl group. Then at least, in the case of the methyl group, eq 10 is approximately obeyed.

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(10) The υ' values which we have calculated are of course related to the *A* values of Okamoto, Taft, and Hine (ref 2, 5, 6) as is shown by the correlation obtained between *A* and υ' (set 1C, Table V). The υ' values were defined in order to be on the same scale as and capable of comparison with the previously defined υ values.

Singlet and Triplet Exciplexes in the Photoreaction of Phenanthrene with Dimethyl Fumarate

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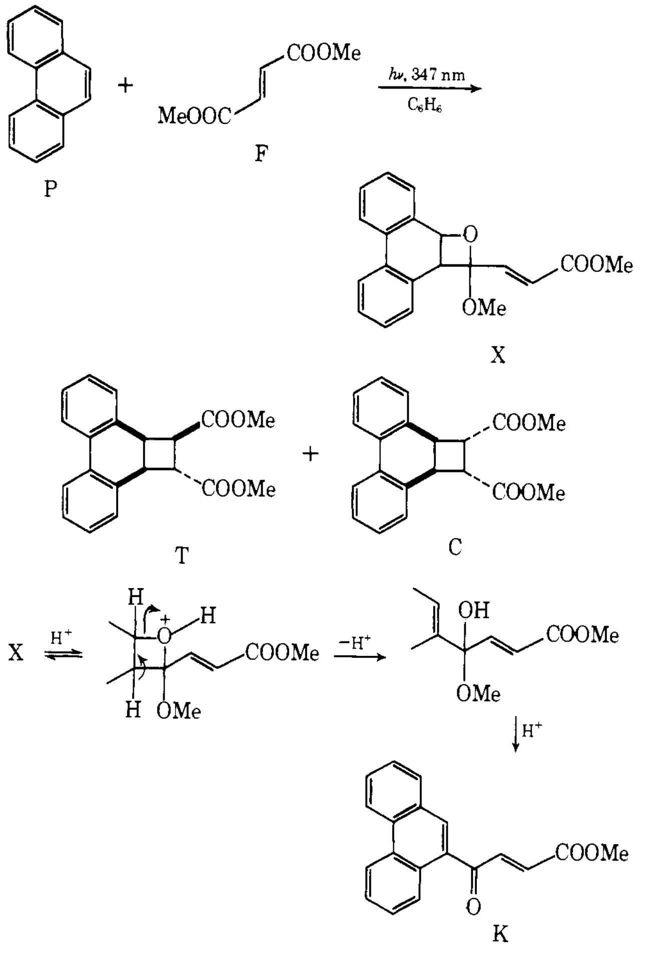
Abstract: The photoreaction of phenanthrene (P) with dimethyl fumarate (F) yields the oxetane (X) and the *trans*- and *cis*-cyclobutanes (T and C). The kinetics of the reaction and quenching experiments are consistent with a diffusion-controlled reaction of singlet excited phenanthrene (P^{*1}) with F to give a weakly emitting singlet exciplex (E^{*1}), which yields X (2.4%) and stereospecifically T (0.1%), intersystem crosses to a triplet exciplex (E^{*3}) (5.3%), and decays to P + F (92.2%). The triplet exciplex (E^{*3}) leads to T (3.2%) and C (1.7%), dissociates to P^{*3} + F (67.2%), and decays to P + F (27.9%, presumably via dissociation of the biradical preceding the formation of T and C).

The spectroscopic and chemical aspects of exciplexes (complexes in the electronically excited state) have attracted considerable interest in recent years.[1] The intermediacy of both singlet and triplet exciplexes has been proposed for several photochemical cycloaddition reactions.[2]

In a preliminary communication,[3] we reported about the involvement of a weakly emitting singlet and a triplet exciplex (which led to oxetane and cyclobutane formation) in the photoreaction of phenanthrene (P) and dimethyl fumarate (F). The intermediacy of a triplet exciplex in the sensitized reaction was also inferred by Caldwell[4] on the basis of rate constants. Recently, Caldwell[5] presented a powerful proof, based on an elegant quenching experiment, that the emitting singlet exciplex is a precursor to the addition products. In this paper, the details of this rather unusual reaction will be presented, together with further evidence for the intermediacy of both exciplexes.

Results and Discussion

From an irradiated benzene solution of phenanthrene (P) (0.05 *M*) and dimethyl fumarate (F) (0.05 *M*) using the filtered output of a Rayonet 3500 Å reactor (Figure 1), the *trans*- and *cis*-cyclobutane derivatives (T and C, respectively), together with the yellow-colored ketone (K), were isolated. The latter compound represents a 1:1 adduct of P and F with the loss of methanol. The formation of this compound could be rationalized if an oxetane (X) were formed as a primary photoproduct and underwent an acid-catalyzed cleavage to (K). To confirm this hypothesis, the reaction was carried out in the presence of traces of pyridine to keep the solution basic. The solution so treated remained colorless on irradiation and turned yellow on subsequent addition of hydrochloric acid. The formation of K on acidification was monitored by absorption spectroscopy. Gas chro-



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