

KINETIC SOLVENT EFFECTS IN THE REACTIONS OF DIPHENYLDIAZOMETHANE WITH ELECTRON ACCEPTORS. CORRELATION BETWEEN ELECTRON AFFINITIES AND THE SLOPES OF THE PLOTS OF  $\log k$  vs SOLVENT BASICITY PARAMETER,  $D_{\pi}$

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**Summary:** Kinetic study of the reactions of diphenyldiazomethane with various electron acceptors were made in six aromatic solvents.  $\log k$  were correlated with the solvent basicity parameter,  $D_{\pi}$ , and the regression slopes were found to be a function of electron affinities.

In our previous paper, we studied the kinetic solvent effects of the reaction of diphenyldiazomethane (DDM) with tetracyanoethylene (TCNE) in 34 aprotic solvents and found that the rate was affected by solvent basicity rather than solvent polarity.<sup>1</sup> Nonbasic solvents like chlorinated alkanes increased the rate, while basic THF and toluene decreased it;  $k_{\text{Chloroform}}/k_{\text{THF}}=157$ . This phenomenon was rationalized by considering the basic solvation of TCNE in the ground state. Keeping this in mind, we proposed a solvent electron donor power,  $D_{\pi}$ , toward a  $\pi$ -acceptor soft acid, using eq. 1, where  $\bar{k}_0$  is the rate constant at 30°C in benzene as reference solvent, and  $\bar{k}$  is the rate constant in another solvent at 30°C. This new parameter is characterized to have relatively large

$$D_{\pi} = \log \bar{k}_0 - \log \bar{k} \quad (1)$$

magnitude for aromatic solvents (soft bases) compared to Koppel-Palm's  $B^2$ , Gutmann's  $DN^3$ , and Kamlet-Taft's  $\beta^4$ , because these conventional parameters were determined by employing rather hard acid probes such as  $\text{CH}_3\text{OD}$  and  $\text{C}_6\text{H}_5\text{OH}$ ,  $\text{SbCl}_5$ , and 4-nitrophenol. Therefore,  $D_{\pi}$  parameter is expected to fit for the physical and chemical properties relating to soft acids as tested in the kinetic solvent effects of Diels-Alder reaction of TCNE and anthracene,<sup>5</sup> and of the decomposition of DDM with  $\text{DDQ}$ .<sup>6</sup> Linear combination with Dimroth and Reichardt's  $E_{\text{T}}^7$  values also succeeded in describing the kinetic solvent effects of the reactions of DDM with chloranil and 2,5-dichloro-*p*-benzoquinone.<sup>8</sup>

We wish to report that  $\log k$  of the reactions of DDM with various  $\pi$ -acceptors were well correlated with  $D_{\pi}$  when aromatic solvents were used, and the

slopes( $m$ ) of these regression equations are the function of the electron affinities(EA) estimated from the CT absorptions<sup>9</sup>. The  $D_{\pi}$  known six aromatic solvents, bromo- ( $D_{\pi}=-1.03$ ), chloro-(-0.903), fluorobenzene(-0.818), benzene(0), ethylbenzene(0.197), and toluene(0.394), were selected for the kinetic studies of the reactions of DDM with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone(1, DDQ), 2,3-dicyano-*p*-benzoquinone(2), tetrafluoro-*p*-benzoquinone(3), tetrachloro-*p*-benzoquinone(4), 2,3,5-trichloro-*p*-benzoquinone(5), 2,6-dichloro-*p*-benzoquinone(6), 2,5-dichloro-*p*-benzoquinone(7), tetrachloro-*o*-benzoquinone(8), TCNE(9), fumaronitrile(10), dimethyl acetylenedicarboxylate(11), and dimethyl fumarate(12). The products were known for DDQ<sup>6</sup>, 4<sup>8</sup>, 7<sup>8</sup>, 8<sup>10</sup>, 9<sup>1</sup>, 10<sup>11</sup>, 11<sup>12</sup>, and 12<sup>13</sup>. The quinones 2 and 3 were found to react only with the C=O bonds as well as DDQ and 4, whereas 5 and 6 provided two types of products arising from the addition of DDM to the C=O and C=C bonds of quinones in analogy with 7. Detailed product analyses will be described elsewhere. The second-order rate constants( $k$ ) were determined at 30°C by monitoring the decrease of the absorp-

Table 1. Correlation of  $\log k$  with  $D_{\pi}$  in the reactions of DDM with electron acceptors

Acceptors	Electron affinities (eV)	$10^3 k$ (benzene) ( $M^{-1} s^{-1}$ )	Coefficients of $D_{\pi}$ ( $=m$ )	R
<u>1</u>	1.95	3050	-1.14	0.999
<u>2</u>	1.7	635	-0.862	0.999
<u>3</u>	(1.50) <sup>a</sup>	37.9	-0.703	0.998
<u>4</u>	1.37	2.66	-0.598	0.998
<u>5</u>	1.3	5.15	-0.490	0.999
<u>6</u>	1.2	3.36	-0.430	0.991
<u>7</u>	1.1	3.38	-0.304	0.995
<u>8</u>	1.55	52600	-0.327	0.974 (0.977) <sup>b</sup>
<u>9</u>	1.8	97.2	-1.00	1.00
<u>10</u>	(1.15) <sup>a</sup>	1.72	-0.363	0.984
<u>11</u>	--	30.4	-0.090	0.833 (0.972) <sup>b</sup>
<u>12</u>	--	7.71	-0.050	0.716 (0.996) <sup>b</sup>

<sup>a</sup> Estimated from eq. 2. <sup>b</sup> R in parenthesis are the values of two parameter correlations ( $n=5$ );  $\log k = -0.340D_{\pi} + 0.00146E_{\pi} + 1.6$  for 8,  $-0.295D_{\pi} - 0.0723E_{\pi} + 0.955$  for 11, and  $-0.253D_{\pi} - 0.0671E_{\pi} + 0.21$  for 12.

tions of acceptors or CT bands with solvents for 1, 2, and 8, and the absorption of DDM for the other acceptor reactions.

Table 1 summarizes the values of  $k$  in benzene solution, the coefficients ( $m$ ) of  $D_{\pi}$  and the correlation coefficients ( $R$ ) of the regression equations of  $\log k$  vs  $D_{\pi}$ , and the electron affinities (EA) of acceptors. Excellent correlations were obtained for  $p$ -quinone reactions as represented for 3 (Fig 1a).

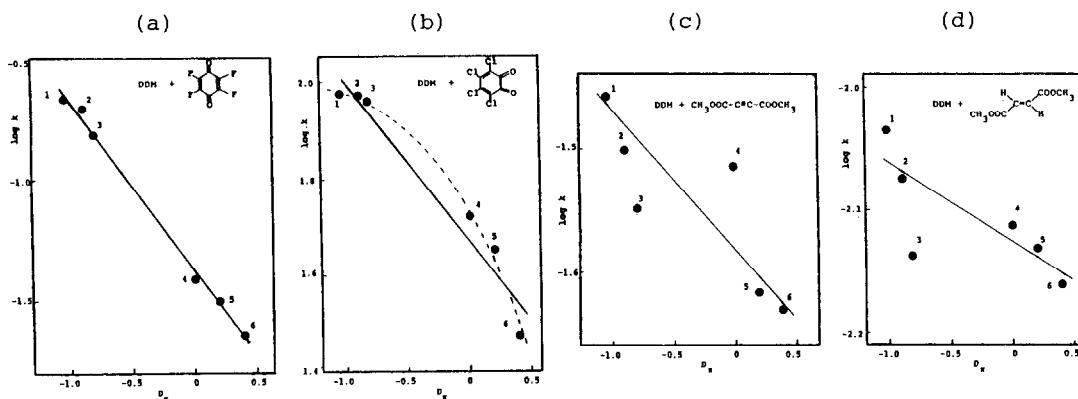


Fig 1. Plots of  $\log k$  vs  $D_{\pi}$  for the reactions of DDM with (a) 3, (b) 8, (c) 11, and (d) 12 in bromo-(1), chloro-(2), fluorobenzene(3), benzene(4), ethylbenzene(5), and toluene(6)

The linear dependence of  $\log k$  on  $D_{\pi}$  indicates that these reactions also undergo the basic solvation in the ground states in a similar manner as does the model TCNE reaction. However,  $o$ -quinone and weaker acceptors, 11 and 12, did not yield good results, though the rates tended to decrease with increasing  $D_{\pi}$  as shown in Fig 1b-d.

Interestingly, the  $m$  of the regression equations were well correlated with the EA of acceptors (eq. 2 and Fig 2). This relationship indicates that

$$m = -0.962EA + 0.743 \quad (n=7, R=0.998) \quad (2)$$

the sensitivity of  $\log k$  on the change of  $D_{\pi}$  is a linear function of the electron affinities of acceptors. From eq. 2, EA of 3 and 10 may be estimated as 1.50 and 1.15 respectively.

Successful application of  $D_{\pi}$  in the reactions with  $p$ -quinones and cyano-

substituted alkenes is ascribed to the predominant basic solvation in ground state compared to the polar solvation of transition state as well as the small change in the polarity of the aromatic solvents used ( $E_T = 33.7-38.1$ ). On the other hand,  $D_\pi$  parameter failed in describing the reactions of weaker acceptor 11 and 12, because the contribution of solvent polarity becomes apparent as exhibited by two parameter treatments of  $\log k$  (Table 1). The deviation for 8 is ambiguous, since the contribution of solvent polarity is negligible.

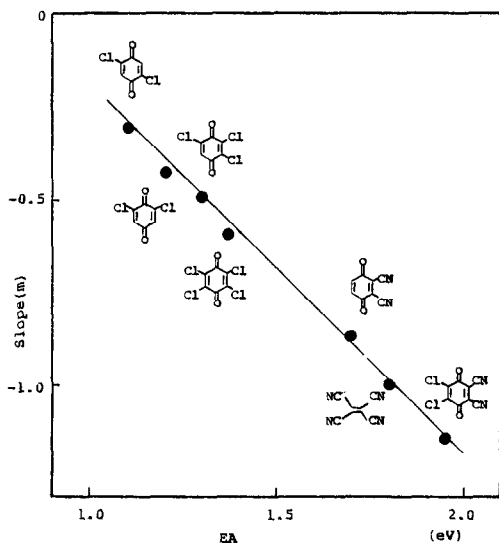


Fig 2. Plot of coefficient of  $D_\pi$  vs EA

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