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Substituent and Solvent Effects in the Reactions of Diaryldiazomethanes with 2,3-Dichloro-5,6-dicyanobenzoquinone

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Kinetic studies have been made of the reactions of fifteen *meta*- and *para*-substituted diphenyldiazomethanes(DDMs) with 2,3-dichloro-5,6-dicyanobenzoquinone(DDQ) in benzene. The second-order rate constants, k, increased with the electron-donability of the substituents, and the value could be correlated with the Yukawa-Tsuno equation: $\log k/k_0 = -2.33(\sigma^0 + 0.47\Delta\bar{\sigma}_R^+) + 0.017$, ($r = 0.996$, 30 °C). The ρ value, −2.33, indicates the development of a positive charge at the diazo carbon in the transition state, while the R value, 0.47, confirms the moderate stabilization of the positive charge by the π-electronic contribution of the para substituents. The rate constants have also been determined for the reaction of diphenyldiazomethane(DDM) with DDQ in 28 aprotic solvents. The effects of solvents can be interpreted in terms of the basicity and the steric nature of the solvents. The products of these reactions were poly(2,3-dichloro-5,6-dicyanohydroquinone benzhydryl ether)s, which were easily convertible into benzophenones and α,α-dimethoxydiphenylmethane, together with 2,3-dichloro-5,6-dicyanohydroquinone, under the influence of water and methanol. These solvolysis products were also obtained in excellent yields in the initial presence of these additives.

In view of the general interest in reactions of diazoalkanes with quinones, most of the synthetic and mechanistic works have been carried out by use of the simplest diazoalkane, *e.g.*, diazomethane.[1] However, little is known of the reactions of aryl- and diaryldiazomethanes[2] with quinones or of kinetic studies of these systems.

We previously reported that chloranil decomposed a variety of substituted diphenyldiazomethanes(DDMs) to produce poly(2,3,5,6-tetrachlorohydroquinone benzhydryl ether)s and that the second-order rate constants were very dependent on the substituents and the solvents.[3] In this paper, we extend our studies of substituent and solvent effects to the kinetics of the reactions of DDMs with 2,3-dichloro-5,6-dicyanobenzoquinone(DDQ).

Results and Discussion

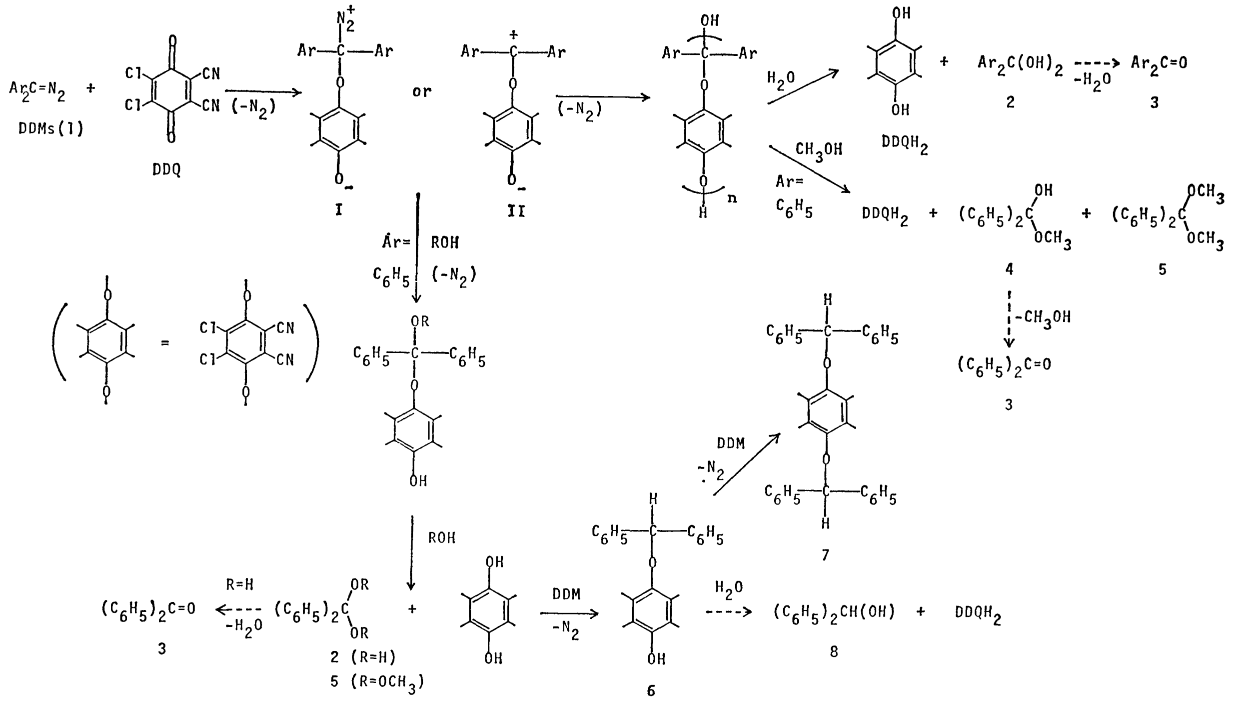
Product Studies. As well as in the case of chloranil,[3] the reactions of fifteen *meta*- and *para*-substituted DDMs with an equimolar amount of DDQ in benzene at 30 °C were much more accelerated with the increase in the electron-donating abilities of the substituents. All these reactions, more or less accompanied by an evolution of N_2, gave resinous products which were highly sensitive to hydroxylic solvents. When these products were hydrolyzed, corresponding benzophenones (**3**) and 2,3-dichloro-5,6-dicyanohydroquinone($DDQH_2$) were isolated in most cases greater than 95%. Moreover, the methanolysis of the product in the case of diphenyldiazomethane(DDM) afforded α,α-dimethoxydiphenylmethane (**5**) in an 81% yield, together with **3** (15%) and $DDQH_2$ (96%). These chemical findings strongly suggest the structure of the 1:1 reaction products to be a hydroquinone polyether linkage similar to that previously considered for the chloranil–DDMs systems.[3] This suggestion is also supported by the representative IR spectrum of the DDM–DDQ system, which exhibited a complete loss of the characteristic carbonyl absorption of DDQ.

The ether linkage may be made up by the successive combination of intermediary diazonium betaines(I) or carbonium betaines(II), as is predicted in Scheme 1. The propagation may be terminated by the action of the residual water present in the solvent. Further action of water and methanol can cause the hydrolytic and methanolytic cleavage of the ether bonds to give *gem*-diols (**2**) and **5**, together with $DDQH_2$; the *gem*-diols are transformed into **3**. In the case of methanolysis, the formation of **3** as a by-product is attributable to the terminal benzhydrol moiety, which primarily degrades into α-methoxy-α-phenylbenzyl alcohol (**4**), which is itself easily convertible into **3**. Therefore, it is possible to estimate the average polymerization degree (n) from the ratio of **5** (81%) to **3** (15%); the value over 5 corresponds to $n = 6$—7.

On the other hand, the initial presence of water and methanol as additives induced solvolysis reactions giving, respectively, **3** and **5**, along with $DDQH_2$. These products are thought to be yielded by the successive nucleophilic attack of these additives on the betaine intermediate, as is also depicted in Scheme 1. These reactions were accompanied by trace amounts of benzhydrol (**8**) and 2,3-dichloro-5,6-dicyanohydroquinone dibenzhydryl ether (**7**) arising from the acid-induced decomposition of DDM by the resulting $DDQH_2$; **8** seems to be afforded by the hydrolysis of 2,3-dichloro-5,6-dicyanohydroquinone benzhydryl ether (**6**).

Apparently, the susceptibility of rates to the substituents, the stoichiometry of the reactions, and the solvolysis evidence all confirm that the present diaryldiazomethanes(DDMs)–DDQ systems proceed through a reaction course similar to that of chloranil systems.[3]

Kinetic Studies. *Substituent Effects*: The reactions of DDMs with DDQ in benzene can be followed spectrophotometrically by monitoring the disappearance of the absorption of DDQ at 408 nm or that of the combined absorptions of both components at 500 nm in the case of nitro-substituted DDMs. These reactions have been found to obey a second-order kinetic law. The rate constants, k, determined for the fifteen *meta*- and *para*-substituted DDMs at various temperatures are listed in Table 1, together



Scheme 1.

TABLE 1. SECOND-ORDER RATE CONSTANTS, AND ACTIVATION PARAMETES FOR THE REACTIONS OF THE SUBSTITUTED DDMs(**1a**—**o**) WITH DDQ IN BENZENE

DDMs	Substituents	$k^{a)}$/l mol^{-1} g^{-1}			ΔH^*/kJ mol^{-1}	ΔS^*/J mol^{-1} K^{-1}
		30 °C	40 °C	50 °C		
1a	p,p'-OCH$_3$	256 (1.11×10^{-1})	—	—	—	—
1b	p-OCH$_3$, p'-CH$_3$	88.4 (4.06×10^{-2})	—	—	—	—
1c	p-OCH$_3$	29.1 (1.95×10^{-2})	—	—	—	—
1d	p,p'-CH$_3$	25.4 (1.42×10^{-2})	—	—	—	—
1e	p-OPh	10.3 (6.85×10^{-3})	—	—	—	—
1f	p-CH$_3$	8.58 (6.67×10^{-3})	—	—	—	—
1g	m-CH$_3$	5.49 (3.41×10^{-3})	8.55	12.1	29.5	−133
1h	p-Ph	3.26 (3.15×10^{-3})	4.74	6.68	26.6	−147
1i	p-H	3.05 (2.66×10^{-3})	4.96	7.72	35.2	−119
1j	p-F	1.88 (2.87×10^{-3})	3.04	4.80	35.6	−126
1k	p-Cl	0.935 (2.07×10^{-3})	1.45	2.28	33.7	−134
1l	m-Cl	0.322 (1.05×10^{-3})	0.505	0.778	33.3	−144
1m	p,p'-Cl	0.283 (—)	0.510	0.831	41.2	−119
1n	m-NO$_2$	0.102 (5.17×10^{-4})	0.188	0.338	46.2	−112
1o	p-NO$_2$	0.0295 (1.15×10^{-4})	0.0594	0.113	52.1	−112

a) The values in parentheses are the second-order rate constants for the reactions of DDMs with chloranil in benzene.

with the activation parameters. This table also includes the comparable kinetic data of the reactions of DDMs with chloranil in benzene at 30 °C. It is noteworthy that the present reactions were much more accelerated with an increase in the electron-releasing abilities of the substituents; the p,p'-dimethoxy substituents caused a *ca.* 9000-fold increase in the rates compared with the p-nitro substituent, though the chloranil system showed only a 960-fold increase.

The dependency of log k/k_0 on the Hammett σ[4] and Brown σ^+[5] constants is shown in Fig. 1. As may be noticed, the additivity of the substituent constants holds for the disubstituted DDMs. Four *meta*-substituted DDMs gave a sufficient linear dependence ($\rho=-2.19$), $r=0.990$ (correlation coefficient) when the simple Hammett equation and normal σ values were used. When correlating all the DDMs and using the normal σ values, we obtained slighlty worse results ($\rho=-2.65$, $r=0.983$). The correlation line curved somewhat upward from the meta line. The replacement of σ by σ^+ displayed a significant curvature with a ρ value of -1.67 ($r=0.976$), wherein the meth-

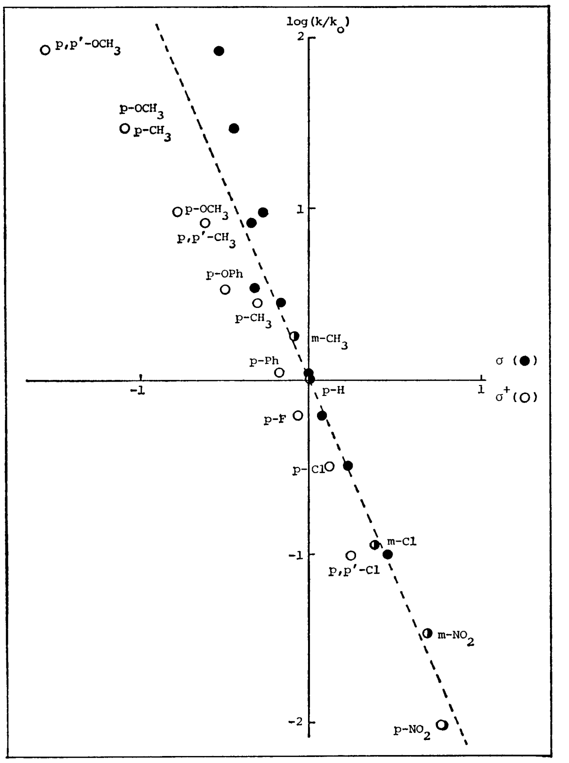


Fig. 1. Plot of $\log k/k_0$ against the Hammett σ(●) and Brown σ^+(○) constants.

oxy substituents induced the marked deviation from the meta line. Thus, the one-parameter equation did not well fit the correlation of *para*-substituted DDMs. We used, therefore, the two-parameter Yukawa-Tsuno equation,[6] $\log k/k_0 = \rho(\sigma^0 + R\Delta\bar{\sigma}_R{}^+)$, where σ^0, R, and $\Delta\bar{\sigma}_R{}^+$ are the normal substituent constant, the resonance reaction constant, and the resonance substituent constant respectively. The two-parameter treatment provided a better correlation (Eq. 1):

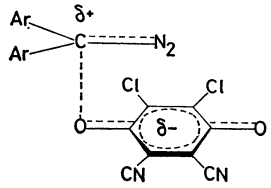
$$\log k/k_0 = -2.33(\sigma^0 + 0.47\Delta\bar{\sigma}_R{}^+) + 0.017 (r=0.996,\ s=0.09,\ n=15). \quad (1)$$

The ρ value of -2.33 is consistent with the development of a positive charge at the diazo carbon in the transition state, while the R value of 0.47 indicates an almost equivalent stabilization of the positive charge by both the inductive and the resonance contributions of the *para* substituents.

When a similar regression analysis was applied to the chloranil–DDMs reactions in benzene (Table 1), a sufficient correlation (Eq. 2) was also obtained with a ρ value of -1.39 and an R value of 0.69:[†]

$$\log k/k_0 = -1.39(\sigma^0 + 0.69\Delta\bar{\sigma}_R{}^+) + 0.0314 (r=0.989,\ s=0.12,\ n=14). \quad (2)$$

A comparison of the Hammett parameters in the two systems is of usefulness in obtaining some information about the transition state. As well as the chloranil–DDMs reactions[3] the present DDQ reactions are postulated to proceed through the polar transition state depicted below, though the polar transition state of 1,3-dipolar addition can not be ruled out. The negatively larger ρ value for DDQ reactions implies that DDQ induces a more positive charge in the diazo carbon, probably because its electron acceptability is stronger than that of chloranil.[7] However, the extent of the resonance stabilization of the positive charge is somewhat lower in DDQ reactions (0.47) than in chloranil reactions (0.69). This discrepancy can be explained by speculating that the higher electron-acceptor ability of DDQ tends to develop more the bond between the diazo carbon and the quinone oxygen. That is, the sp^2 hybridization of the diazo carbon is reduced, and the effect of resonance contribution is thereby lessened, compared to the case of chloranil.



Solvent Effects: In a previous paper, we discussed the kinetics of the reaction of DDM with chloranil in several aprotic solvents.[3] The kinetic solvent effects were tentatively interpreted in terms of the stabilization of the initial state relative to the transition state. We have now extended these studies of solvent effects to the kinetics of the present reaction. As is shown in Table 2, the rates were much more accelerated in the halogenated solvents, while they were decelerated in tetrahydrofuran or toluene; the k values for chloroform and carbon tetrachloride are *ca.* 110—160 times greater than for toluene. Nonpolar carbon tetrachloride is also noticiable for bringing about a 10—50-fold increase in the rate compared to the polar acetonitrile and acetone. These kinetic results imply that the reaction rate is primarily influenced by the solvation of the initial state rather than by that of the transition state for which the polar-activated complex was deduced from the kinetic substituent effects. This situation is represented in the free-energy profile, where the stronger solvation of initial reactants overcomes the accelerating solvation of the present polar-activated complex, consequently increasing the free activation energy (Fig. 2).

Since DDQ is a strong electron-acceptor, like chloranil and TCNE,[7] such specific solute-solvent interactions as the formation of a charge-transfer complex may be expected, especially in the solvents with a high basicity.[8] Therefore, we attempted to correlate $\log k$ with some of the solvent-basicity parameters, *e.g.*, $\Delta\nu_D$,[9] β,[10] and DN.[11] The symbols have the following meanings: $\Delta\nu_D$ is defined as the relative difference between the O–D absorption band of methanol-*d* observed in a given solvent and that in benzene; β, as the hydrogen-bonding acceptor basicity, and DN (donor number), as the negative ΔH values for 1:1 adduct formation between antimony pentachloride and electron-pair donor solvents in 1,2-dichloroethane.

[†] We have reported in our previous paper[3] that in the THF medium the chloranil systems also gave an excellent correlation with a somewhat large negative ρ value of -1.67 and a substantially equal R value of 0.66.

Table 2. Rate constants and activation parameters for the reaction between DDM and DDQ in aprotic solvents, with solvent basicity parameters

	Solvents	k/l mol^{-1} s^{-1}			ΔH^*	ΔS^*	$\Delta\nu_D$	β	DN
		30 °C	40 °C	50 °C	kJ mol^{-1}	J mol^{-1} K^{-1}			
1	Chloroform	169	—	—	—	—	−17	—	—
2	Dichloromethane	146	—	—	—	—	−12	—	—
3	Carbon tetrachloride	136	—	—	—	—	−21	—	0
4	1,2-Dichloroethane	134	—	—	—	—	2	—	0
5	Diisopropyl ether	56.8	—	—	—	—	75	0.466	—
6	Bromobenzene	39.2	—	—	—	—	−1	0.062	—
7	Chlorobenzene	30.8	—	—	—	—	−2	0.071	—
8	Nitrobenzene	30.3	—	—	—	—	21	—	4.4
9	Fluorobenzene	27.6	—	—	—	—	—	—	—
10	Methyl chloroacetate	25.1	—	—	—	—	27	—	—
11	Dibutyl ether	12.8	18.7	24.8	24.3	−144	—	0.453	—
12	Acetonitrile	11.2	14.3	18.2	17.2	−170	49	0.31	14.1
13	Diethyl ether	10.3	—	—	—	—	78	0.466	19.2
14	Propionitrile	7.85	10.6	12.9	17.6	−170	52	—	16.1
15	1,2-Dimethoxyethane	4.20	7.27	11.5	38.4	−107	71	0.405	24
16	Benzene	3.05	4.96	7.72	35.2	−119	0	0.1	0
17	Acetone	2.91	—	—	—	—	64	0.478	17
18	Ethyl methyl ketone	2.58	—	—	—	—	57	—	—
19	1,4-Dioxane	2.22	3.08	4.56	26.8	−150	77	0.369	14.8
20	Dimethoxymethane	2.10	—	—	—	—	—	—	—
21	Ethyl acetate	1.81	2.74	3.93	29.0	−145	39	0.446	17.1
22	Ethylbenzene	1.56	2.44	4.78	43.1	−99.5	4	—	—
23	Isopropyl acetate	1.38	2.02	3.00	29.0	−147	—	—	—
24	Methyl acetate	1.34	2.16	3.42	35.6	−125	36	0.454	16.5
25	Tetrahydrofuran	1.27	2.24	3.46	38.2	−117	90	0.550	20
26	Propyl acetate	1.13	1.92	3.05	37.8	−119	—	—	—
27	Tetrahydropyran	1.12	—	—	—	—	93	0.544	—
28	Toluene	1.03	1.85	3.20	43.6	−101	2	0.112	—

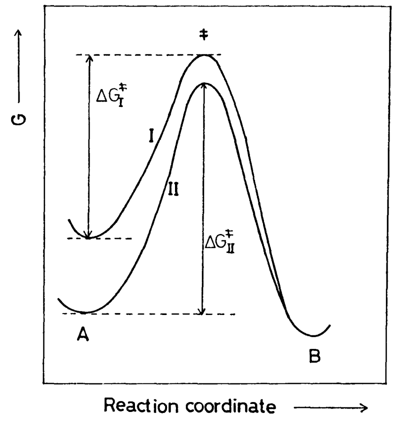


Fig. 2. Schematic free energy profiles for the reaction with non-solvated(I) and solvated(II) reactants (preferential solvation of the initial reactants). $\Delta G^\ddagger_\mathrm{I}$, $\Delta G^\ddagger_\mathrm{II}$=Free activation energy in nonpolar(I) and polar solvents(II) respectively. A=Initial reactants; ‡=activated complex; B=products.

The values of $\Delta\nu_D$, β, and DN are available for 23, 15, and 13 of our solvents respecitvely, and inspection (Table 2) shows that the reaction tends to be fast in weakly basic solvents and slow in strongly basic solvents.

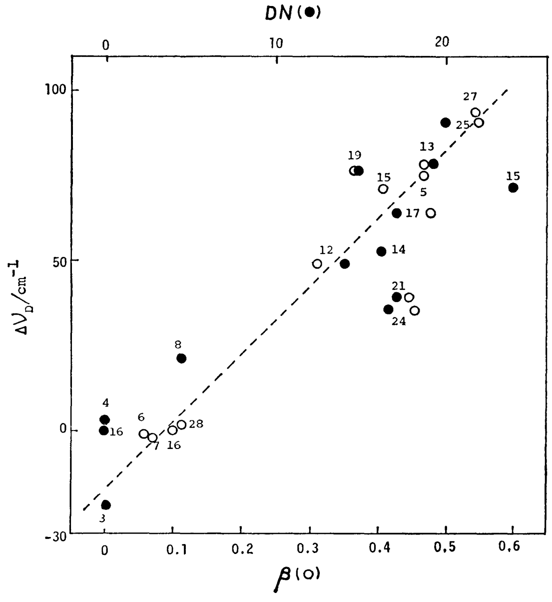


Fig. 3. Relationships between $\Delta\nu_D$ and β, and DN; for point numbers, see Table 2.

A comparison of these parameters substantially presented the linear relationship shown in Fig. 3. We adopted the widely available $\Delta\nu_D$ values as the solvent

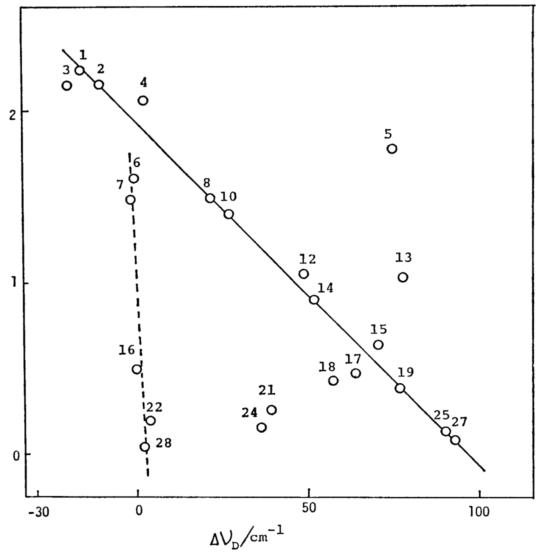


Fig. 4. Plot of log *k* against $\Delta\nu_D$; for point numbers, see Table 2.

basic parameter. As is shown in Fig. 4, a plot of log *k* against the $\Delta\nu_D$ values provided two correlation groups, excluding six solvents (Solv. Nos. 5, 13, 17, 18, 21, 24). The first solvent group, including aliphatic chlorinated solvents, nitriles, and cyclic ethers, moderately decreased the logarithmic rate with the increase in the solvent basicities. The regression analysis gave an excellent correlation (Eq. 3, solid

$$\log k = -0.0196\Delta\nu_D + 1.92 (r=0.991,\ s=0.005,\ n=12) \qquad (3)$$

line). The second group, consisting of five aromatic solvents, brought about a steeper decrease (slope −0.259, broken line). The correlation equation (r= 0.848), however, is not so good, probably because the $\Delta\nu_D$ values of these aromatic solvents are too narrow (ranging from −2 to 4 cm^{-1}) to avoid the uncertainty due to the error (±1 cm^{-1}) in the measured shift of O–D stretching.

These phenomena confirm that the present reaction is essentially governed by the extent of the interaction between solvents and DDQ in the initial state. Two solvent groups are given because of the difference in the solvent basic nature. Of the solvents, alkyl halides are σ-donors; ethers, nitriles, and ketones are *n*-donors, and aromatic hydrocarbons are π-donors.[12] According to the HSAB concept,[13] DDQ is a soft acid π-acceptor and prefers to bind soft bases, such as benzene and toluene. Therefore, the specific stability of the π-donor–π-acceptor complexes between the aromatic solvents and DDQ seems to give a separate correlation line from the first solvent group. These aromatic solvents are strong bases toward such π-acceptors as DDQ, while they are weak toward a typical hard acid methanol, as judged by the small $\Delta\nu_D$ values. However, nitrobenzene was an exceptional aromatic solvent, probably because the negatively charged nitro group acts overwhelmingly as an associating site.

It can also be seen in Fig. 4 that the log *k* values for the solvents containing carbonyl groups (Nos. 17, 18, 21, 24) and for diethyl ether (No. 13) and diisopropyl ether (No. 5) are smaller and larger respectively than called for by Eq. 3. We assume that these carbonyl solvents possess, to some extent, a softness toward DDQ, the property of which can not be evaluated by the interaction with hard acid methanol-*d*. Methyl chloroacetate, however, belongs to the first solvent group because the chlorine substituent weakens the basicity. The upper deviation of diethyl and diisopropyl ethers is attributable to the steric hindrance, which is of some importance in estimating the strength of the solvent–DDQ interaction. A bulky substituent adjacent to the oxygen atom undoubtedly causes an increase in the rate, probably because of the poor solvation of DDQ. This phenomenon can be understood in terms of the Taft steric constants,[14] E_S, which predict the present increase in *k* in the series of diisopropyl ether (E_S=−0.47)>dibutyl ether (−0.39)>diethyl ether (−0.07).

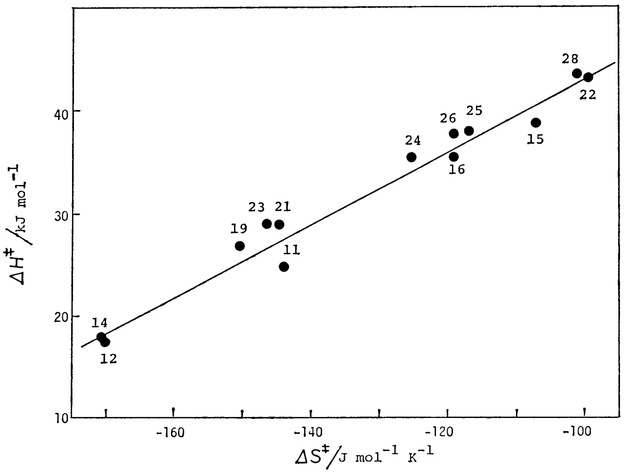


Fig. 5. Plot of ΔH^{*} *vs.* ΔS^{*}; for point numbers, see Table 2.

With regard to the enthalpies and entropies of activation, a plot of ΔH^{*} against ΔS^{*} displayed a linear correlation (r=0.98, Fig. 5). The ΔH^{*} values vary from 17.2 to 43.6 kJ mol^{-1} in going from acetonitrile to toluene, while the ΔS^{*} values vary from −99.5 to −170 J mol^{-1} K^{-1} in going from ethylbenzene to acetonitrile. The larger ΔH^{*} values for toluene and ethylbenzene are indicative of the high stabilization of the DDQ molecule, consistent with the favorable π-π donor acceptor interaction in the initial state, by which the negatively smaller ΔS^{*} values of these solvents can be explained.

Experimental

The IR and NMR spectra were recorded on Hitachi 215 and Varian EM-360 spectrometers respectively. The UV spectra were observed with Hitachi 323 and JASCO UVIDEC 505 instruments.

Materials. All the diaryldiazomethanes were made by the oxidation of the corresponding hydrazones with yellow mercury(II) oxide, as has previously been described.[15] The physical properties of these diazoalkanes were listed in previous papers.[3,16] The 2,3-dichloro-5,6-dicyanobenzoquinone(DDQ) was of commercial origin and was recrystallized from dichloromethane; orange yellow needles, mp 213 °C. All the solvents were dried and purified according to the standard procedures.[17]

Kinetic Measurements. The kinetic data were obtained according to the standard spectrophotometric methods. Solutions for kinetic experiments were prepared separately just before use in a volumetric flask equipped with a stopper. The DDQ solution (10^{-5}—10^{-3} mol dm^{-3}) was introduced into a stoppered quartz optical cell (10 mm) and kept at the given temperature within ±0.1 °C in a thermostat-controlled cell-holder of a Hitachi 323 spectrophotometer. The reaction was initiated by the quick addition of the requisite volume of a DDM slution(10^{-5}—10^{-3} mol dm^{-3}), which had been preheated in a water bath to the same temperature as the above cell-holder. The change in the maximum absorption (408 nm, $\varepsilon=2750$) of DDQ in benzene was conveniently monitored over at least two half-lives in the cases of the DDMs (**1a**—**m**), for these diazoalkanes and the products are essentially transparent at this wavelength. In the cases of nitrosubstituted DDMs(**1n**—**o**), the additive absorption of these diazoalkanes(**1n**; $\varepsilon=122$, **1o**; $\varepsilon=290$) and DDQ($\varepsilon=361$) at 500 nm in benzene was followed. The measurements in the other solvents were made by following the appropriate absorption of DDQ in the regions of 380—410 nm. The second-order rate constants, k, were determined graphically from the plots of $\ln\{b(a-x)/a(b-x)\}/(a-b)$ against the time, where a and b are the initial concentrations of the DDMs or DDQ respectively, x being the consumed DDMs or DDQ. The rate constants were reproducible within ±3%(usually two determinations).

Reactions of Diaryldiazomethanes(DDMs) with DDQ in Benzene. General Procedures: A benzene solution (10 ml) of diphenyldiazomethane(DDM) (0.50 g, 2.58 mmol) was added, all at once, to a solution of DDQ (0.59 g, 2.60 mmol) in benzene (20 ml). The purple color of DDM suddenly disappeared with the vigorous evolution of N_2. After stirring for 1 h (one overnight standing for the nitro-substituted DDMs), the solvent was evaporated *in vacuo* to give an essentially colorless, resinous product, the IR spectrum of which showed no absorption in the C=O region. The product was then treated with a ten-fold excess of water or methanol for 10 min, with occasional shaking and dried under reduced pressure. The pasty residue thus obtained was triturated with 50 ml of benzene. Filtration gave $DDQH_2$ (0.56—0.57 g, 94—96%). The filtrate was washed with aqueous sodium carbonate and dried over anhydrous sodium sulfate. The subsequent evaporation of benzene gave benzophenone (0.45 g, 96%) in the case of treatment with water or α,α-dimethoxydiphenylmethane(**5**) (0.48 g, 81%) and benzophenone (70 mg, 15%) in the case of treatment with methanol. The relative yields of **5** and benzophenone were determined by means of the NMR spectrum of the product mixture, while pure **5** was obtained by fractional crystallization from pentane. The benzophenones and **5** were identified by a comparison of the IR and NMR spectra with those of authentic samples.[3]

Reaction of Diphenyldiazomethane(DDM) with DDQ in H_2O–Benzene. A benzene solution (10 ml) of DDM (0.50 g, 2.58 mmol) and H_2O (0.23 g, 13 mmol) was added, all at once, to a solution of DDQ (0.59 g, 2.60 mmol) in benzene (20 ml). After stirring for 1 h, the removal of the solvent, followed by column chromatography(silica gel), gave 2,3-dichloro-5,6-dicyanohydroquinone dibenzhydryl ether(**7**) (35 mg, 5% based on the DDM used), and benzophenone (0.40 g, 85%) with a petroleum ether–benzene mixture, and then $DDQH_2$ (0.49 g, 83%) and benzhydrol(**8**) (30 mg, 6%) with a benzene–ether mixture. The product, **7**, had a mp of 190—191 °C (from benzene) (lit,[18] mp 189—190 °C), IR(KBr): 2235, 1412, 993, 928, and 695 cm^{-1}; NMR (δ, $CDCl_3$): 6.67(2H, s) and 7.33(20H, s); Found: C; 72.94, H; 4.15, N; 4.94%. Calcd for $C_{34}H_{22}Cl_2N_2O_2$: C; 72.72, H; 3.95, N; 4.99%. Compound **8** was identified by a comparison of its IR and NMR spectra with those of a commercial sample.

Reaction of DDM with DDQ in CH_3OH–Benzene. A benzene solution (10 ml) of DDM (0.50 g, 2.58 mmol) and CH_3OH (0.42 g, 13 mmol) was added, all at once, to a solution of DDQ (0.59 g, 2.60 mmol) in benzene (20 ml). After stirring for 1 h, the reaction mixture was evaporated *in vacuo* and the pasty residue was triturated with benzene (50 ml). Filtration gave pure crystalline $DDQH_2$ (0.54 g, 91%). The filtrate part was divided in equal parts and was examined by two different methods. One part was washed with aqueous sodium carbonate (5%), dried over sodium sulfate, and evaporated to dryness to give crystalline **5** (0.26 g, 87%). The other part was evaporated, followed by column chromatography(silica gel) to give **7** (30 mg, 4%) and benzophenone (0.20 g, 85%) with a petroleum ether–benzene mixture, and **8** (15 mg, 6%) with a benzene–ether mixture. Thus, acetal **5** was completely changed into benzophenone on silica-gel-column chromatography.

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