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# Kinetic Solvent Effects in the Decomposition of Diphenyldiazomethane with Chloranil and 2,5-Dichloro-*p*-benzoquinone

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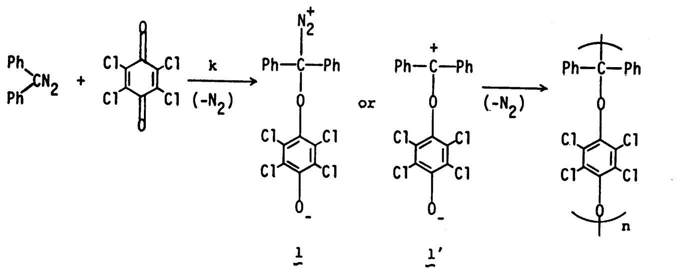
A kinetic study was made of the reactions of diphenyldiazomethane (DDM) with chloranil and 2,5-dichloro-*p*-benzoquinone (DCQ) at 30 °C in 20 and 22 aprotic solvents respectively (19 solvents are common). The chloranil reaction gave poly(tetrachlorohydroquinone benzhydryl ether) alone, obeying the second-order kinetic law. On the other hand, the DCQ reaction afforded bicyclic dione and poly(2,5-dichlorohydroquinone benzhydryl ether), also obeying the second-order kinetic law. All these rate constants generally increased with the solvent polarity and decreased with the solvent basicity. The kinetic solvent effects can be interpreted in terms of the effects of the polarity and the basicity of the solvents respectively to the transition and to the initial states. Thus, the multiple linear correlations of the logarithmic rate constants with a suitable function of the polarity and the basicity of the solvents are fairly successful. It was found that the basicity is more pronounced in the chloranil reaction than in the DCQ reaction, whereas the reverse can be said for the solvent polarity. These results were compared to those of the reactions of DDM with 2,3-dichloro-5,6-dicyanobenzoquinone and tetracyanoethylene.

In our previous paper,[1)] we proposed an empirical basicity parameter, $D_\pi$, based on the kinetic solvent effects on the reaction of diphenyldiazomethane (DDM) with tetracyanoethylene (TCNE) as a typical $\pi$-acceptor. The $D_\pi$ was found to be preferable to the conventional solvent basicity parameters, such as Kagiya's $\Delta\nu_D$[2)] Kamlet-Taft's $\beta$ scale,[3)] and Gutmann's *DN* (donor number),[4)] to describe the solvent effects in the kinetics of the various reactions involving $\pi$-acceptor soft acids. For example, the correlation of log *k* with $D_\pi$ for the 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ)-DDM reaction over a wide range of aprotic solvents was highly successful ($r$=0.977).[1)] We have now extended the work to the chloranil- and 2,5-dichloro-*p*-benzoquinone (DCQ)-DDM reactions in order to examine further the application of $D_\pi$ in the interpretation of the kinetic solvent effects. In this paper, we also discuss the results in comparison with those for the DDM-TCNE and DDM-DDQ systems.

## Results and Discussion

*The Dependence of the Rate Constants on the Properties of the Aprotic Solvents in the Reactions of Diphenyldiazomethane with Chloranil.* The chloranil–DDM reaction is found to afford poly(tetrachlorohydroquinone benzhydryl ether) by way of a diazonium or carbonium betaine intermediate, **1** or **1′** (Scheme 1).[5)] The second-order rate constants over a wide range of aprotic solvents are shown in Table 1, together with the $D_\pi$[1)] and the solvent polarity parameters, the Kirkwood function of the dielectric constants $\varepsilon$, $f(\varepsilon)=(\varepsilon-1)/(2\varepsilon+1)$,[6)] and Dimroth and Reichardt's $E_T$ values.[7)] An inspection of the results shows that the rates did not correlate well only with the usual solvent basicity or polarity parameter. Dipolar solvents, *e.g.*, nitro compounds and nitriles, tended to increase the rates, while the basic aromatic hydrocarbons and cyclic ethers decrease them. A preliminary correlation of log *k* with the conventional basicity parameters, such as $\Delta\nu_D$, the $\beta$ scale, and *DN*, yielded worse results because of the marked deviation of the aromatic hydrocarbons: $\log k=-0.0048\Delta\nu_D-1.97$ (correlation coefficient($r$)=0.35, data points ($n$)=18), $\log k=-0.198\beta-2.23$ ($r$=0.10, $n$=11), and $\log k=-0.028DN-1.76$ ($r$=0.45, $n$=11). However, a plot of log *k* against $D_\pi$ values showed a better correlation, suggesting the stabilization of the initial state as a result of the basic solvation of the chloranil molecule; $\log k=-0.536D_\pi-2.23$ ($r$=0.826, $n$=20) (Fig. 1). The six nonpolar aromatic hydrocarbons and derivatives (Solv. Nos. 9, 10, 11, 18, 21, and 23) were well correlated (slope=−0.600, $r$=0.998), but the dipolar solvents displayed an inverted U-shaped deviation. The apparent acceleration by the dipolar solvents may be attributed to the stabilization of the transition state by the dipole-dipole interaction. The effects of the substituents on the rate supported the polar transition state with a partial positive charge on



Scheme 1.

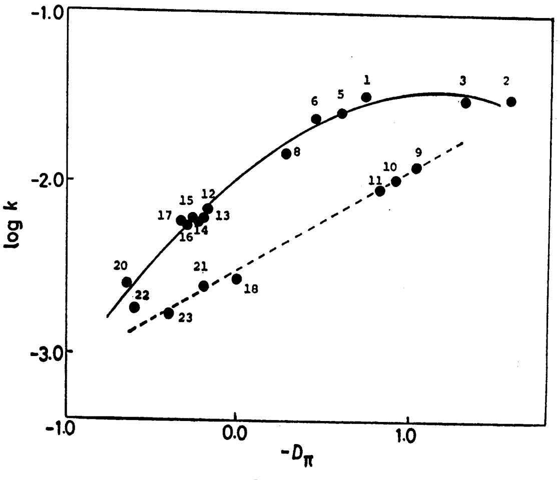


Fig. 1. Plot of log *k* against $D_\pi$.

TABLE 1. SECOND-ORDER RATE CONSTANTS ($1\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$) FOR THE DECOMPOSITIONS OF DIPHENYLDIAZOMETHANE WITH CHLORANIL AND 2,5-DICHLORO-*p*-BENZOQUINONE IN VARIOUS SOLVENTS AT 30 °C, WITH THE SOLVENT BASICITY AND THE POLARITY PARAMETERS

| Solvent | Chloranil | 2,5-Dichloro-*p*-benzoquinone | | | | $D_\pi$ [b] | $E_T$ [c] | f(ε) [d] |
|---|---|---|---|---|---|---|---|---|
| | $10^3 k$ | 2/3 [a] | $10^3 k_{obsd}$ | $10^3 k_1$ | $10^3 k_2$ | | | |
| 1 Nitromethane | 32.3 | 0.670 | 15.9 | 6.44 | 9.46 | −0.724 | 46.3 | 0.479 |
| 2 Chloroform | 30.7 | 0.535 | 15.5 | 5.40 | 10.1 | −1.56 | 39.1 | 0.359 |
| 3 1,2-Dichloroethane | 30.5 | 0.611 | 14.3 | 5.65 | 9.25 | −1.22 | 41.9 | 0.431 |
| 4 Dichloromethane | — | 0.611 | 13.5 | 5.12 | 8.38 | −1.30 | 41.1 | 0.420 |
| 5 Nitrobenzene | 24.4 | — | — | — | — | −0.583 | 42.0 | 0.479 |
| 6 Acetonitrile | 23.4 | 0.711 | 13.4 | 5.57 | 7.83 | −0.440 | 46.0 | 0.480 |
| 7 Benzonitrile | — | 0.618 | 11.1 | 4.24 | 6.86 | −0.398 | 42.0 | 0.471 |
| 8 Propionitrile | 14.5 | 0.676 | 10.8 | 4.35 | 6.45 | −0.277 | 43.7 | 0.473 |
| 9 Bromobenzene | 12.1 | 0.681 | 7.26 | 2.94 | 4.32 | −1.03 | 37.5 | 0.373 |
| 10 Chlorobenzene | 10.1 | 0.685 | 6.32 | 2.57 | 3.75 | −0.903 | 37.5 | 0.377 |
| 11 Fluorobenzene | 8.90 | 0.690 | 5.56 | 2.27 | 3.29 | −0.818 | 38.1 | 0.373 |
| 12 Ethyl methyl ketone | 6.43 | 0.496 | 8.02 | 2.66 | 5.36 | 0.177 | 41.3 | 0.461 |
| 13 Methyl acetate | 6.29 | 0.848 | 5.23 | 2.40 | 2.83 | 0.196 | 40.0 | 0.396 |
| 14 Cyclohexanone | 5.69 | 0.501 | 7.01 | 2.34 | 4.67 | 0.243 | 40.8 | 0.460 |
| 15 Acetone | 5.68 | 0.685 | 7.48 | 3.04 | 4.44 | 0.261 | 42.2 | 0.464 |
| 16 Ethyl acetate | 5.34 | 0.710 | 4.65 | 1.93 | 2.72 | 0.289 | 38.1 | 0.385 |
| 17 Propyl acetate | 5.30 | 0.697 | 5.26 | 2.16 | 3.10 | 0.337 | 37.5 | 0.385 |
| 18 Benzene | 2.66 | 0.954 | 3.38 | 1.65 | 1.73 | 0.000 | 34.5 | 0.230 |
| 19 Tetrahydropyran | — | 0.670 | 3.39 | 1.36 | 2.03 | 0.539 | — | 0.377 |
| 20 Tetrahydrofuran | 2.43 | 0.634 | 2.37 | 0.919 | 1.45 | 0.639 | 37.5 | 0.407 |
| 21 Ethylbenzene | 2.42 | 0.706 | 3.07 | 1.27 | 1.80 | 0.197 | — | 0.241 |
| 22 1,4-Dioxane | 1.79 | 0.655 | 2.93 | 1.16 | 1.77 | 0.590 | 36.0 | 0.223 |
| 23 Toluene | 1.65 | 0.864 | 2.46 | 1.14 | 1.32 | 0.394 | 33.9 | 0.239 |

a) The product ratios (**2**/**3**) were determined by means of high-performance liquid chromatography; the yield of **3** was taken as the amount of benzophenone after the hydrolysis of **3**. b) Relative logarithmic rate constants of the reaction of diphenyldiazomethane with TCNE in benzene as the reference solvent and in a given solvent; Ref. 1. c) Dimroth and Reichardt's $E_T$ values; Ref. 7. d) Kirkwood function; $f(\varepsilon)=(\varepsilon-1)/(2\varepsilon+1)$; Ref. 6.

the diazo-carbon: $\log k/k_0=-1.67(\sigma^0+0.66\Delta\bar{\sigma}_R{}^+)+0.009$,[5] at 30 °C in THF. However, the correlation of log *k* with f(ε) ($r$=0.69) or $E_T$ ($r$=0.74) was less satisfactory than that with $D_\pi$. This implies that the chloranil reaction is more dependent on the basic property ($D_\pi$) of the solvents.

To obtain a more satisfactory regression, let us examine the multiple correlation of log *k* with $D_\pi$ values and with $E_T$ or f(ε) as the solvent polarity parameter. The two parameter equations consisting of linear combination of $D_\pi$ and $E_T$ or f(ε) improved the correlation, as may be seen in Eq. 1 for 19 solvents and in Eq. 2 for 20 solvents:

Chloranil-DDM reaction:

$$\log k = -4.77 - 0.421 D_\pi + 0.0650 E_T \quad (r=0.977,\ s=0.0945,\ n=19), \tag{1}$$

$$\log k = -3.16 - 0.450 D_\pi + 2.45 f(\varepsilon) \quad (r=0.963,\ s=0.120,\ n=20). \tag{2}$$

The Kirkwood function, f(ε), appears less successful than $E_T$, as is shown by the values of *r* in Eqs. 1 and 2. A plot of log *k*(obsd) *vs.* log *k*(calcd) according to Eq. 1 is shown in Fig. 2.

*The Dependence of the Rate Constants on the Properties of the Aprotic Solvents in the Reactions of Diphenyldiazomethane with 2,5-Dichloro-*p*-benzoquinone (DCQ).* The DCQ decomposed DDM to give two products, bicyclic dione (**2**) and poly(2,5-dichlorohydroquinone benzhydryl ether) (Scheme 2).[8] The formation of **2** may be explained as arising from the initial product, pyrazoline, followed by the loss of $N_2$; the polyether may then be thought to be made up by the polymerization of a diazonium or carbonium betaine intermediate, like **1** or **1′**. The participation of the betaine intermediate was evidenced by the isolation of 2,5-dichloro-4-

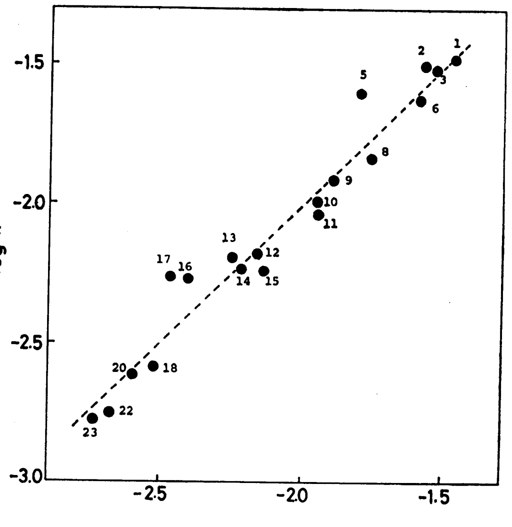
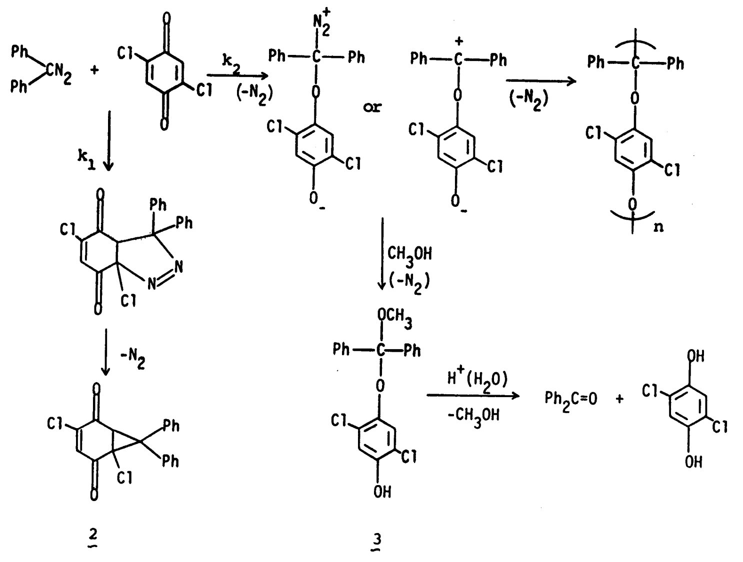


Fig. 2. Plot of log *k* (obsd) against log *k* (calcd) according to Eq. 1, for point numbers, see Table 1.



Scheme 2.

[(methoxy)diphenylmethoxy]phenol (**3**) in the reaction carried out in the presence of a trace amount of $CH_3OH$;[8] **3** was easily hydrolyzed into benzophenone and 2,5-dichlorohydroquinone. Thus, the yield was taken as the amount of benzophenone. However, no essential change was noticed in the observed rate constant or in the yield of **2** between the reaction in the absence and in the presence of a trace of $CH_3OH$ as an additive, as exemplified by a 1,2-dichloroethane solution.[8] Therefore, we made product and kinetic studies of the solvents containing a 5 molar excess of $CH_3OH$ with respect to DDM, and then the total and the relative yields of **2** and benzophenone after the hydrolysis were conveniently determined by means of high-performance liquid chromatography. The combined yields of **2** and **3** amount to more than 95% in all the solvents used. The observed second-order rate constants ($k_{obsd}$) were divided into the individual rate constants, $k_1$ and $k_2$, for the paths leading, respectively, to **2** and **3**, by combining them with their relative yields. The kinetic data and the relative product yields are also shown in Table 1.

An examination of the results shows that, although the variation in the rate constants with the changing solvent is considerably low, $k_1$ and $k_2$ depend on both the basicity and the polarity of the solvents, as in the case of a chloranil reaction; $\log k_1 = -1.35 + 0.584 \log k$ ($r=0.962$, $n=19$) and $\log k_2 = -1.05 + 0.644 \log k$ ($r=0.946$, $n=19$), where $k$ is the rate constant in the chloranil-DDM reaction. For a comparison of $k_1$ and $k_2$, a similar but slightly greater dependence of $k_2$ on the properties of the solvents can be anticipated from the linear correlation: $\log k_2 = 0.392 + 1.08 \log k_1$ ($r=0.973$, $n=22$).

For example, a single-parameter correlation of the logarithmic rate constants with the $D_\pi$, $E_T$, and $f(\varepsilon)$ values is as follows: $\log k_1 = -2.65 - 0.289 D_\pi$ ($r=0.769$, $n=22$), $\log k_1 = -4.87 + 0.0582 E_T$ ($r=0.797$, $n=20$), $\log k_1 = -3.38 + 2.05 f(\varepsilon)$ ($r=0.673$, $n=22$), and $\log k_2 = -2.48 - 0.311 D_\pi$ ($r=0.743$, $n=22$), $\log k_2 = -5.02 + 0.0664 E_T$ ($r=0.807$, $n=20$), $\log k_2 = -3.37 + 2.46 f(\varepsilon)$ ($r=0.727$, $n=22$). A comparison of the $r$ values of these correlations indicates that both $k_1$ and $k_2$ are more affected by the solvent polarity ($E_T$) than by the basicity ($D_\pi$). This trend is the opposite of that found in the chloranil reaction. Attempts to obtain more satisfactory correlations were done using two parameters, $D_\pi$ and $E_T$ or $f(\varepsilon)$. The results are shown as Eqs. 3 and 4 for $\log k_1$ and as Eqs. 5 and 6 for $\log k_2$:

DCQ–DDM reaction:

$$\log k_1 = -4.45 - 0.205 D_\pi + 0.0460 E_T \quad (r = 0.962,\ s = 0.0176,\ n = 20), \tag{3}$$

$$\log k_1 = -3.24 - 0.240 D_\pi + 1.55 f(\varepsilon) \quad (r = 0.912,\ s = 0.110,\ n = 22), \tag{4}$$

$$\log k_2 = -4.57 - 0.218 D_\pi + 0.0535 E_T \quad (r = 0.953,\ s = 0.090,\ n = 20), \tag{5}$$

$$\log k_2 = -3.22 - 0.249 D_\pi + 1.94 f(\varepsilon) \quad (r = 0.926,\ s = 0.113,\ n = 22). \tag{6}$$

As the case of the chloranil reaction, both the equations involving $D_\pi$ and $E_T$ gave better correlations than the corresponding expressions involving $D_\pi$ and $f(\varepsilon)$. The superiority of the $E_T$ paramater may be ascribed to the intrinsic combined measure of solvent polarity and acidity,[9] by which the specific solvation of the transition state with the negatively charged quinone moiety is effected. Furthermore, a comparison of the coefficients of $D_\pi$ and $E_T$ in Eqs. 3 and 5 shows that the **3** path receives more influence of the solvent polarity than does the **2** path; the absolute coefficients of $D_\pi$ increased *ca.* 6%, but the corresponding values of $E_T$ increased *ca.* 16%, in going from Eq. 3 to Eq. 5. The plots of $\log k_1$ (obsd) *vs.* $\log k_1$ (calcd) and $\log k_2$ (obsd) *vs.* $\log k_2$ (calcd), according to, respectively, Eqs. 3 and 5, are shown in Fig. 3. The greater susceptibility of the **3** path to the solvent polarity than the **2** path can be ascribed to the more-charged transition state suggested by the kinetic substituent effects: $\log k_1 = -2.15 - 1.55\sigma$ and $\log k_2 = -2.03 - 1.85\ (\sigma^0 + 0.515\ \Delta\bar{\sigma}_R^+)$.[8]

*Comparison of the Kinetic Solvent Effects of the Chloranil–*

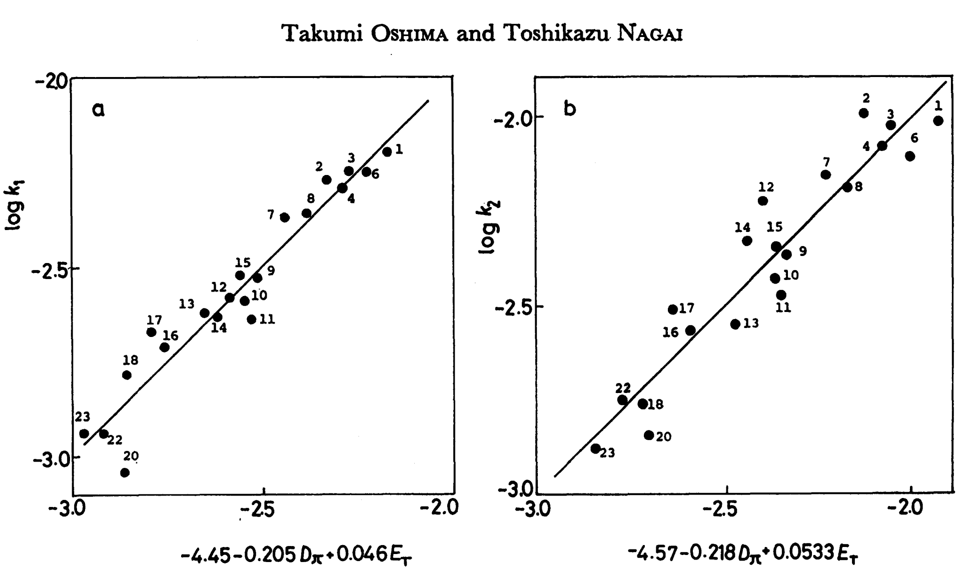


Fig. 3. a) Plot of log $k_1$ (obsd) *vs.* log $k_1$ (calcd) according to Eq. 3. b) Plot of log $k_2$ (obsd) *vs.* log $k_2$ (calcd) according to Eq. 5, for point numbers, see Table 1.

*DDM and DCQ–DDM Reactions with Those of the DDQ–DDM and TCNE–DDM Reactions.* We are now in a position to compare the kinetic solvent effects in the decomposition of DDM with various $\pi$-acceptor acids, *i.e.*, chloranil, DCQ, DDQ, and TCNE.

In formulating the $D_\pi$ scale in 34 aprotic solvents,[1] we used the difference between the logarithmic rate constants of the TCNE–DDM reaction in benzene (as a reference solvent) and the solvent at 30 °C, so the log *k* can be described by this modified form:

TCNE–DDM reaction:

$$\log k = -1.01 - D_\pi, \tag{7}$$

where the intercept is log *k* for benzene.

This empirical parameter could successfully be applied to the kinetics of the DDQ–DDM reaction in 26 aprotic solvents at 30 °C.[1] The least-square correlation equation is as in Eq. 8:

DDQ–DDM reaction:

$$\log k = 0.623 - 1.10D_\pi$$
$$(r = 0.977, s = 0.161, n = 26). \tag{8}$$

A comparison of the intercepts and the slopes in Eqs. 7 and 8 indicates that the DDQ reaction is *ca.* 30 times faster in the benzene solution ($D_\pi = 0$) and depends slightly more on the solvent basicity than the TCNE reaction. On the contrary, the chloranil and DCQ reactions, both having substantially the same orders of rates, gave rates about 50 times lower in benzene and showed a less effective contribution of the $D_\pi$ compared to the TCNE reaction, as may be seen in the coefficients of $D_\pi$ in Eqs. 1, 3, and 5. It should also be noted that these equations are characteristic in incorporating the solvent-polarity parameter.

The solvation effects in both initial and transition states must be taken into account in order to understand the influence of the solvent on the rate. In the initial state, the basic solvation of the $\pi$-acceptor acids is the chief factor influencing the rate constants, as exemplified by the UV blue shifts and the appearance of the charge-transfer absorption of TCNE[10,11] and chloranil[12] on going to more basic solvents† (Table 2). One can easily notice the parallelism between the absolute coefficients of $D_\pi$ and the electron affinity of these $\pi$-acids in the order of DDQ (1.95 eV)>TCNE (1.80)> chloranil (1.37)>DCQ (1.1).[13] This means that the extent of the basic solvation can be related to the $\pi$-acceptor ability of these acids. On the other hand, the transition states may be stabilized by the dipole-dipole interaction in the polar media, since the kinetic substituents effects of all these reactions suggest charged transition states.

Here again, let us summarize the Hammett parameters, $\rho$, with the correlation fashion: TCNE reaction; −2.67 (with Brown's $\sigma^+$)[14], DDQ; −2.33 (Yukawa-Tsuno equation),[15] chloranil; −1.67 (Yukawa-Tsuno equation),[5] and DCQ; −1.85 (for the path giving **3**, Yukawa-Tsuno equation) and −1.55 (for path giving **2**, with normal $\sigma$).[8] If the $\rho$ values may be taken as a suitable estimate of the charge appearance of the transition state, the TCNE and DDQ reactions are more likely to be stabilized by the polar solvent than are the chloranil and DCQ reactions. An examination of Eqs. 1—8, however, shows that the DDQ reaction is satisfactorily correlated only with $D_\pi$, while the chloranil and DCQ reactions are well expressed by a linear combination of $D_\pi$ and a polarity parameter, such as $E_T$ and f($\varepsilon$). This apparent discrepancy can be easily explained by the relative significance of the stabilizations in the initial and transition states in comparison with that for the model TCNE–DDM reaction. By definition, the $D_\pi$ parameter inherently reflects the influence of the solvent, not only on the initial state, but also on the transition state of the TCNE–DDM reaction. The free energies of the solvation of the initial state ($\Delta G_B$) are, of course, greater than those of the transition state ($\Delta G_P$), as was demonstrated earlier by the statistically better correlation of the logarithmic rate constants with the conventional basicity param-

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† By contrast, the $\pi$-$\pi^*$ absorption of DDM in the ultraviolet region remained essentially unchanged during such a variation of solvents, reflecting the lower solvation of DDM.[1]

TABLE 2. SOLVENT EFFECTS ON THE UV ABSORPTION SPECTRA OF TCNE AND CHLORANIL AT 25 °C

| Solvent | TCNE $\lambda_{max}$/nm (log $\varepsilon$) | | Chloranil $\lambda_{max}$/nm (log $\varepsilon$) | |
|---|---|---|---|---|
| Chloroform | 267.7(4.16) | 277.6(4.15) | 292.0(4.35) | 374.0(2.37) |
| Dichloromethane | 267.4(4.13) | 277.7(4.09) | | |
| Acetonitrile | 262.5(4.20) | 271.5(4.16) | 287.0(4.32) | 367.5(2.39) |
| Propionitrile | 263.0(4.22) | 272.3(4.18) | | |
| Ethyl acetate | 259.0(4.18) | 270$^{a)}$ (4.08) | 287.0(4.27) | 364.0(2.40) |
| Propyl acetate | 258.5(4.19) | 270$^{a)}$ (4.09) | | |
| Tetrahydrofuran | 260.6(4.08) | 270$^{a)}$ (4.02)<br>318(3.49)$^{b,c)}$ | 283.5(4.23) | 330$^{a)}$ (3.16)$^{e)}$ |
| 1,4-Dioxane | 259.5(3.98) | 350(3.27)$^{b,c)}$ | 285.5(4.20) | 330$^{a)}$ (3.20)$^{e)}$ |
| Fluorobenzene | | | 285.5(4.12) | 330$^{a)}$ (3.27)$^{e)}$ |
| Benzene | | 384(3.55)$^{b,d)}$ | 283.5(4.16)<br>346$^{b,f)}$ | 332(3.33)$^{b,e)}$ |
| Toluene | | 406(3.52)$^{b,d)}$ | 286.5(4.19)<br>365$^{b,f)}$ | 362(3.27)$^{b,e)}$ |

a) Shoulder. b) Due to charge-transfer absorption. c) Values taken from Ref. 10; measured in $CHCl_3$ at 25 °C. d) Values taken from Ref. 11; measured in $CH_2Cl_2$ at 22 °C. e) Measured in $7.0\times10^{-4}$ mol/l. f) Values taken from Ref. 12; measured in cyclohexane at 18—20 °C.

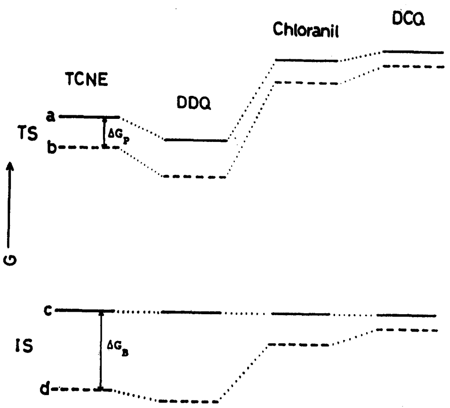

Fig. 4. Solvent effect upon reactants and transiton states, TS: transition states in nonpolar (a) and in polar (b) solvents; IS: initial states in nonbasic (c) (depicted arbitrarily in the same level) and basic (d) solvents.

eters, such as $\Delta\nu_D$, $\beta$, and $DN$, than those with $E_T$ and f($\varepsilon$).[1] This situation is schematically shown in Fig. 4, together with the other cases of DDQ, chloranil, and DCQ reactions.

In the case of the DDQ reaction, the lack of a polarity parameter and the slightly excess sensitivity to the $D_\pi$ may, therefore, be ascribed to essentially the same $\Delta G_P/\Delta G_B$ ratios, but to somewhat greater individual values, compared to the TCNE reaction. On the other hand, the incorporation of the polarity parameter in the chloranil and DCQ reactions is the result of the significant decrease in the basic solvation; therefore, the relative role of $\Delta G_p$ may be pronounced with respect to $\Delta G_B$.

Recently, Krygowski and Fawcett proposed a similar two-parameter regression with the aid of $E_T$ and $DN$, where $Q$ is a physicochemical quantity and $\alpha$ and $\beta$ are the regression coefficients:[9]

$$Q = Q_0 + \alpha E_T + \beta DN.$$

The application of this empirical equation to the present chloranil and DCQ reactions, however, resulted in a much worse correlation because $DN$ is inadequate to describe the softness of aromatic solvents.

## Experimental

The bicyclic dione (**2**): benzophenone ratios and the overall yields of **2** and benzophenone were determined by means of JASCO trirotor high-performance liquid chromatography (HPLC), using biphenyl as the internal standard. The HPLC analysis was carried out at room temperature using a 250 mm×4.6 mm column packed with ODS (octadecylsilane) on silica gel; methanol–water (7 : 3 by volume); flow rate, 1 ml/min. The UV detector was calibrated at 245 nm with standard mixtures of known concentrations of benzophenone, **2**, and biphenyl. The relative retention times were as follows: benzophenone (0.53), **2** (0.68), and biphenyl (1.0).

*Materials.* The diphenyldiazomethane (DDM) was synthesized as has been described by Smith and Howard[16] and recrystallized from light petroleum; mp 29—30 °C. The chloranil was of commercial origin and was recrystallized twice from benzene; mp 290 °C. The 2,5-dichloro-*p*-benzoquinone (DCQ) was prepared according to the procedure described by Ling[17] and was recrystallized from ethanol; mp 164—166 °C. All the solvents were dried and purified according to the standard procedures.[18]

*Kinetic Measurements.* The values of $k$ were determined spectrophotometrically as has previously been described[5,8] by the use of Hitachi 323 and JASCO UVIDEC-505 instruments. The absorption cells were thermostated at 30±0.1 °C with a Haake circulator. The mean deviations for $k$ were ±3% (usually two determinations).

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