flushed with purified argon, and the cell was then inserted in a temperature-controlled compartment of a Beckman D.U. spectrophotometer. After temperature equilibration a finely powdered sample, 10–20 mg, of the quinol ether IIIa or IIIf was added to solution *via* a microsalt funnel which had been in thermal contact with the liquid in the cell. Upon addition the quinol ether immediately dissolved and the liquid in cell was stirred with a small capillary which had been previously suspended into the cell. The absorbance of the solution, Ab_t, at 4500 Å was then determined as a function of time. The absorbance of the solution at times corresponding to 8–10$t_{1/2}$, Ab_∞, agreed within ±3% with that calculated from the initial concentrations of IIIa and IIIf. The value of the molar extinction coefficient from 2,5-di-*t*-butylquinone at 4500 Å is equal to 32.5 ± 0.3 M^{-1} cm^{-1}. The first-order rate constant, k_{-2}, was then calculated from plots of log $[Ab_\infty - Ab_t]$ *vs.* time. Such plots were linear for over 4$t_{1/2}$ in all cases.

Kinetic Study of the Reaction (IIIb–IIId) with 2,5-Di-*t*-pentylhydroquinone. Solutions of III and 2,5-di-*t*-pentylhydroquinone or di-*t*-butylhydroquinone in chlorobenzene were placed in 10-ml volumetric flasks, flushed with purified argon, and the stoppers sealed with paraffin wax. The flasks were placed in the constant-temperature bath and allowed to equilibrate. At various intervals of time the flasks were removed and quenched to room temperature. Aliquots were then withdrawn and delivered into solutions of NaI in glacial acetic acid under a CO_2 atmosphere. After standing for 20 min at room temperature the liberated iodine was titrated with standardized thiosulfate solution. Plots of log [(titer)$_\infty$ − (titer)$_t$]/(titer)$_\infty$ *vs.* time were linear for over 3 half-lives and the value of (titer)$_\infty$, ($\sigma - 10t/2$), agreed within ±3% with the value calculated from the initial concentration of III. Blank experiments with III and with the hydroquinone yielded negligible titers.

Acknowledgment. The authors wish to acknowledge the excellent technical assistance rendered by Mrs. Jennie Chen and Mr. F. C. Ferris during the course of the study.

Rates and Isotope Effects in the Quinone Oxidation of Leuco Triphenylmethane Dyes[1]

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Abstract: Rates and hydrogen isotope effects in the oxidation of some leuco dyes of the form of 4,4′-bisdimethylamino-*n*-X-triphenylmethane by quinones (mostly halogenated *p*-benzoquinones) have been studied. For the case of the 4′′-dimethylamino substituent (chloranil) the rates were studied as a function of temperature in acetonitrile and in methanol with both hydrogen and deuterium in the tertiary position. In acetonitrile the rate constant of the hydrogen compound is given by $k_H = 1.2 \times 10^5 \exp(-8150/RT)$ and the isotope effect by $k_H/k_D = 0.041 \exp(3360/RT)$. The isotope effects were less precise in methanol, and were somewhat smaller, but the A_H/A_D factor was still less than unit. Rates and isotope effects are presented for several other quinones and leuco dyes and electronic and perhaps small steric effects were observed. The oxidation with 2,3-dichloro-5,6-dicyanoquinone was too fast to measure, but competitive measurements showed that the reaction had about the same ρ as with chloranil but a smaller isotope effect. The results are entirely consistent with tunneling in this hydride-transfer reaction.

The study of hydrogen-transfer reactions has proved interesting in part because they represent the simplest examples of nucleophilic, radical, and electrophilic substitution, and also because extra information is readily available from the hydrogen isotope effect. Of these, the electrophilic substitutions, or hydride transfer, has been subject to the least study.

The rates of several hydride transfers are readily measured, although some are extremely fast;[4] they therefore cover much the same very wide range of rates characteristic of proton-transfer reactions. There is a further uncertainty in hydride-transfer reactions not common to proton-transfer reactions, namely the geometry of the transition state. In proton transfers, the linear transition state appears to be energetically favorable, but arguments have been presented for triangular transition states from some hydride-transfer reactions.[5] These arguments are more plausible than rigorous, and can hardly be taken as convincing.

The subject for the present work is the oxidation of substituted leuco malachite greens by chloranil and other quinones. This reaction has been shown to be quantitative[6] in dimethylformamide, and the kinetics have been studied in methanol solution, in which the oxidation of dye is quantitative, but the chloranil is used to excess by a side reaction.[7] The study of this presumed hydride transfer was made more interesting because large isotope effects have been reported in the oxidation of some triphenylmethanes by carbonium ions.[8]

Results

The reaction studied is the reaction 1. Also shown are the compounds studied, with the exception of a few quinones not derived from *p*-benzoquinone. As noted before,[7] the reaction is first order in each of the reagents, independent of acid concentration, and in acetonitrile is independent of water or oxygen content of the sol-

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[1] The Mechanism of Hydride Transfer. III. From portions of Ph.D. Theses of R. H. Grinstein (1961) and J. M. Perry (1965).

[2] Robert A. Welch Foundation Predoctoral Fellow, 1963–1965.

[3] Humble Oil and Refining Co. Fellow, 1960–1961.

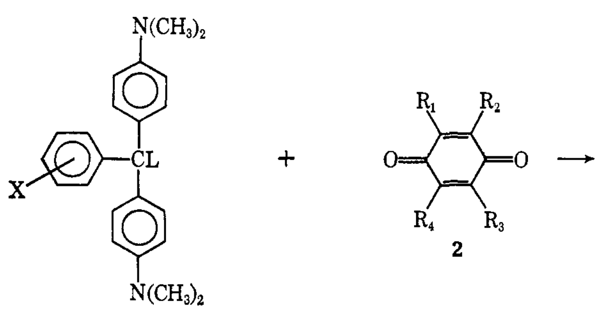
[4] P. D. Bartlett, F. E. Condon, and A. Schneider, *J. Amer. Chem. Soc.*, **66**, 1531 (1944).

[5] (a) M. F. Hawthorne and E. S. Lewis, *ibid.*, **80**, 4296 (1958); b) E. S. Lewis and R. H. Grinstein, *ibid.*, **84**, 1158 (1962).

[6] J. H. Jones, M. Dolinsky, K. S. Heine, Jr., and M. C. Staves, *J. Assoc. Offic. Agr. Chemists*, **38**, 977 (1955).

[7] C. D. Ritchie, W. F. Sager, and E. S. Lewis, *J. Amer. Chem. Soc.*, **84**, 2349 (1962).

[8] H. J. Dauben, private communication.



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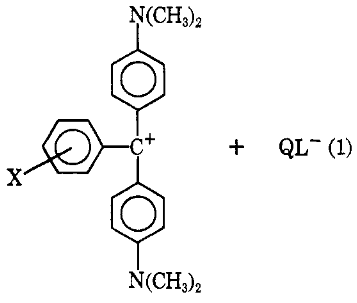
1a, X = p-N(CH$_3$)$_2$; L = H or D
b, X = o-(OCH$_3$); L = H or D
c, X = m-Cl; L = H or D
d, X = H; L = H or D
e, X = p-NO$_2$; L = H

2a, R$_1$ = R$_2$ = R$_3$ = R$_4$ = Cl
b, R$_1$ = R$_2$ = R$_3$ = R$_4$ = Br
c, R$_1$ = R$_2$ = R$_3$ = R$_4$ = I
d, R$_1$ = R$_2$ = Br; R$_3$ = R$_4$ = Cl
e, R$_1$ = R$_4$ = Br; R$_2$ = R$_3$ = Cl
f, R$_1$ = R$_3$ = Br; R$_2$ = R$_4$ = Cl
g, R$_1$ = R$_4$ = Cl; R$_2$ = R$_3$ = F
h, R$_1$ = R$_2$ = Cl; R$_3$ = R$_4$ = CN



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vent. We therefore conclude that we are dealing with a one-step hydride-transfer mechanism, although the argument lacks rigor. The reaction in methanol is complicated in the only case studied, with Q = tetrachloro-p-benzoquinone, by solvolysis of the quinone; this occurs at a rate not entirely negligible compared to the rate of reaction 1. In acetonitrile, chloranil is quite stable and the reaction rate is accurately second order up to large extents of completion. Most runs were made with excess chloranil, so that the reaction followed a first-order course. In methanol the rates reported are initial rates measured as before,[7] and the side reaction caused a substituent, isotope, and temperature dependent error of small but variable magnitude. Table I shows these results in methanol for leuco crystal violet **1a** with chloranil **2a**. Because of this and other errors, only representative examples of the data from the thesis of Grinstein are here presented. The rate constant for **1**, L = D, is called k_D in this paper.

Table I. Oxidation of Leuco Crystal Violet by Chloranil in Methanol

Temp, °C[a]	$k_H \times 10^2$, M^{-1} sec^{-1} [b]	$k_D \times 10^2$, M^{-1} sec^{-1} [b,c]	k_H/k_D[c]
2.7	9.68	0.856	11.3
14.7	19.8	2.00	9.9
29.9	43.2	5.27	8.2
44.7	89.5	12.6	7.1

[a] The temperature control involved a circulatory system and the actual cell temperatures may have been slightly closer to room temperature than those shown, although attempts were made to allow for this problem. [b] Reproducibility of rate contants was in all cases good, usually better than 1%. [c] The error introduced by the methanolysis of chloranil is most serious in the slower k_D measurements. No correction is made for incomplete deuteration of the leuco dye.

The rather large isotope effects fit eq 2 with satisfactory precision, but the error due to the side reaction mentioned above, and one possible error in temperature control mentioned in footnote *a* of Table I, make these Arrhenius constants less than completely convincing.

$$k_H/k_D = 0.345 \exp(1933/RT) \qquad (2)$$

The remaining results were therefore obtained in acetonitrile which was much more satisfactory from aspects of solubility and stability of all reagents and products, and the dye was not strongly adsorbed onto the cell surfaces, as it was from less polar but otherwise satisfactory solvents. Furthermore, the purity of the solvent did not seem to be a factor, since the only difference between various carefully purified materials and a technical grade was that the less pure grades gave an orange color with chloranil. Ammonium acetate, a likely contaminant, gave a similar color. After distillation from phosphorus pentoxide, no color was produced, and the same rate constants were obtained with all solvent samples.

Table II shows some substituent effects in this solvent with both chloranil **2a** and bromanil **2b**. No correction on k_D for incomplete deuteration is necessary, since the reaction was carried out to a large extent of completion, so that k_D is determined by the limiting slope of the pseudo first-order plot even in the presence of substantial amounts of undeuterated material. The course of the reaction with chloranil in fact constituted the best method of analysis of a mixture of deuterated and undeuterated material. No sample used for determination of k_D was less than 98% deuterated, however.

Table II. Rate of Oxidation of Substituted Leuco Malachite Greens by Quinones in Acetonitrile

X in compd **1**	Substitution in p-benzoquinone	k_H, M^{-1} sec^{-1} [a]	k_D, M^{-1} sec^{-1}	k_H/k_D[a]
H	Cl$_4$[b]	2.05×10^{-2}	1.80×10^{-3}	11.4
H	Br$_4$[c]	1.26×10^{-2}		
o-OCH$_3$	Cl$_4$	1.81×10^{-2}	1.51×10^{-3}	11.9
o-OCH$_3$	Br$_4$	1.40×10^{-2}	1.10×10^{-3}	12.7
m-Cl	Cl$_4$	1.06×10^{-2}	8.95×10^{-4}	11.8
p-(CH$_3$)$_2$N	Cl$_4$	1.27×10^{-1}	1.08×10^{-2}	11.4
p-(CH$_3$)$_2$N	Br$_4$	8.14×10^{-2}	6.08×10^{-3}	13.4

[a] Errors estimated from reproducibility are ±2-3%. [b] Tetrachloro-p-benzoquinone **2a**. [c] Tetrabromo-p-benzoquinone **2b**.

Table III shows the temperature dependence of the rate constants and isotope effects in the oxidations of leuco crystal violet **1a** by chloranil in acetonitrile. The temperatures given are those in the cell controlled and measured as described in the Experimental Section, and the relative temperatures justify the number of significant figures given, although the relation to the International Temperature Scale is only good to within 0.1°. No reason for the discrepancy of the isotope effect in the first entry is known, but the discrepancy is entirely in the value of k_H, which is much smaller than the value predicted by the Arrhenius equation defined by the other points.

Table III. Temperature Dependence of the Rate Reaction of Leuco Crystal Violet with Chloranil

Temp, °C	$k_H \times 10^2$, M^{-1} sec^{-1} [a]	$k_D \times 10^2$, M^{-1} sec^{-1} [a]	k_H/k_D
9.96	5.23 ± 0.22	0.380 ± 0.004	13.7
14.88	7.45 ± 0.02	0.51.5 ± 0.007	14.7
19.83	9.96 ± 0.37	0.738 ± 0.012	13.1
24.91	12.7 ± 0.4	1.08 ± 0.05	11.8
29.84	15.4 ± 0.3	1.40 ± 0.01	11.01
35.44	19.4 ± 0.7	1.96 ± 0.006	9.9
13.3	7.12		
13.6	7.45		
13.8		0.445	
25.15	12.6		

[a] The ± figures are deviations from the mean of usually two, occasionally more, runs. Single runs are given without this error estimate.

Table IV. Rates of Oxidation of Leuco Crystal Violet **1a** by Various Quinones at 25° in Acetonitrile

Quinone[a]	k_H, M^{-1} sec^{-1}	k_H/k_D
Tetrachloro **2a**	1.27×10^{-1}	11.4
Tetrabromo **2b**	8.14×10^{-2}	13.4
2,3-Dibromo-5,6-dichloro **2d**	9.29×10^{-2}	11.8
2,5-Dibromo-3,6-dichloro **2f**	8.07×10^{-2}	11.8
2,6-Dibromo-3,5-dichloro **2e**	8.46×10^{-2}	12.0
2,5-Dichloro	$\sim 1 \times 10^{-2}$ [b]	
2,5-Dichloro-3,6-difluoro **2g**	2.1×10^{-2} [c]	13.2 (±2.5)
Tetrachloro-*o*-benzoquinone	3.21[d]	3.1
2,3-Dichloro-5,6-dicyano **2h**	$>10^5$ [e]	6.96[f]
Tetrachlorodiphenoquinone	7.5×10^{-1} [g]	9.8
Tetrabromodiphenoquinone	3.23[g]	12.9
Tetraiodo **2c**	4.4×10^{-2} [g]	11.6

[a] Unless otherwise named, these are substituted in *p*-benzoquinones. [b] Reaction kinetically complex, possibly because of semiquinone formation. All three dichloro-*p*-benzoquinones gave within the large experimental uncertainty about the same rates. [c] This quinone was somewhat unstable in the solvent and was also of questionable identity, see Experimental Section. [d] Crystal violet was oxidized by excess quinone, and presumably this occurs during the run, hence neither the rate constants nor especially the isotope effect are very accurate. [e] Both k_H and k_D were found too fast to measure, the value presented is an estimate based on the concentrations used and the time to start measurements. [f] Determined competitively two ways, see text. [g] None of these quinones was soluble enough to give reliable rates; there is no reason to suspect gross errors in the rates.

The rates of oxidation of leuco crystal violet by some other quinones in acetonitrile at 25° are shown in Table IV. The first five entries represent entirely satisfactory kinetics, the remainder are less quantitatively reliable for various reasons indicated in the footnotes. In addition to these, several other quinones gave a color presumed to be **3**($X = p\text{-N(CH}_3)_2$) but were not further investigated for various reasons: *p*-benzoquinone and dichloro-*p*-xyloquinone (reaction detected only in concentrated solutions at elevated temperatures), and 2,5-dichloro-3,6-diacetamido-*p*-benzoquinone and 2,5-dibromo-3,6-diiodo-*p*-benzoquinone (not soluble enough). Unsubstituted diphenoquinone was rapidly destroyed in acetonitrile and did not give the crystal violet color.

The isotope effect with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (**2h**) was determined competitively by two different methods. In one, a sample of a mixture of 38.00% leuco crystal violet with 62.00% of the deuterated compound was dissolved in acetonitrile and mixed very rapidly with a solution of an amount of quinone necessary to oxidize 68.2% of the dye. The residual leuco dye was isolated, recrystallized, and the protium content determined by the kinetic method using oxidation with excess chloranil. The final protium content (1.08%) then allowed calculation of the isotope effect using the equation given by Melander,[9] which gave $k_H/k_D = 6.99$ with an uncertainty of ±0.07 from the estimated errors in the isotopic analysis.

The second method, also competitive, depended on the determination of the relative rate of oxidation of two leuco dyes, leuco crystal violet **1a**, L = H, and 4′′-nitroleuco malachite green **1e**, L = H. The relative rates were determined by adding an insufficiency of the quinone to a known mixture of the leuco dyes and determining the yields of the two dyes from the ultraviolet absorption. The leuco crystal violet was oxidized 31.9 times as fast as the nitro compound. The relative rates of reaction of the deuterated leuco crystal violet **1a**, L = D, and the nitro compound **1e**, L = H, were determined by the same spectrophotometric method, and the deuterated compound was oxidized 4.58 times as fast as the nitro compound. These data then yield $k_H/k_D = 6.96$ in gratifyingly close agreement with the other determination. To our knowledge, a hydrogen isotope effect has not before been determined by a competitive method not requiring an isotopic analysis.

Discussion

The results in methanol solution of Table I do show that the isotope effect is large and that it is strongly temperature dependent. The small A_H/A_D term fits Bell's criterion for an important tunnel correction.[10] The uncertainties are such that the quantitative interpretation is not very reliable. We shall not make a further attempt.

The substituent effects in Table II are worthy of note for several reasons. The difference in isotope effects from those in Table I are not very large, and those in Table I may be a little small because no correction for the protium content was made. Thus, the solvent change introduces no drastic new effects.

The rate of the protium compound in methanol is about 3 times as great as it is in acetonitrile; this arises from a somewhat higher activation energy, combined with slightly larger A factor, as shown below in the Arrhenius equations, derived from Table III: $k_H^{\text{MeOH}} = 1.8 \times 10^6 e^{-9180/RT}$; $(k_D^{\text{MeOH}} = 5.0 \times 10^6 e^{-11,080/RT})$; $k_H^{\text{MeCN}} = 1.2 \times 10^5 e^{-8130/RT}$; $k_D^{\text{MeCN}} = 2.92 \times 10^6 e^{-11,520/RT}$.

The parentheses around the equation for k_D^{MeOH} indicate that known errors contribute most heavily to it. Part of the difference between the Arrhenius terms in the two solvents lies in a different definition of concentration. In methanol the concentrations are expressed as moles per liter measured at 25°; the solutions were then cooled and heated as required for the rate measurements. In acetonitrile the concentrations are expressed as moles per liter at the temperature of measurement. The difference is trivial for aqueous solutions, but the large coefficient of thermal expansion of acetonitrile makes a substantial difference between the concentration expressions. The coefficient of expansion of the volumetric glassware was neglected.

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(9) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1960, p 49.

(10) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, New York, 1959, p 211.

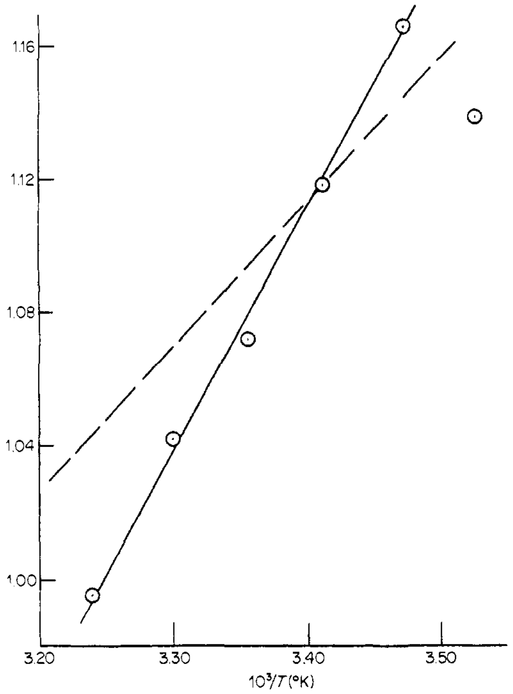

Figure 1. Arrhenius plot for the isotope effect in the chloranil oxidation of leuco crystal violet. Solid line is that for eq 3, the dashed line is that with the smallest acceptable classical intercept, eq 4.

The observed isotope effects were also fitted to the Arrhenius equation, giving results close to those obtained by dividing the above equations. In acetonitrile, the result is shown in eq 3. The Arrhenius constants

$$k_{\mathrm{H}}/k_{\mathrm{D}} = 0.041e^{3360/RT} \tag{3}$$

suggest tunneling even more strikingly than the less precise ones in methanol.

The experimental error is estimated to be about 40% in $A_{\mathrm{H}}/A_{\mathrm{D}}$ from the fit of eq 3 to the experimental data. However, a point at the lowest temperature was omitted because k_{H} failed to fit the Arrhenius equation at this temperature, even when it was included in the least-squares calculation, by more than two standard deviations. We demonstrate the reality of the small $A_{\mathrm{H}}/A_{\mathrm{D}}$ and the justification for omitting the one point, in Figure 1, in which the experimental data of Table III are plotted. The line corresponding to eq 3, as well as the alternative line of eq 4, which has the minimum classi-

$$\log k_{\mathrm{H}}/k_{\mathrm{D}} = \log (0.5) + \frac{1904}{2.303}RT \tag{4}$$

cally allowed $A_{\mathrm{H}}/A_{\mathrm{D}}$ factor, are shown. It is seen that even with weight given to the lowest temperature point, it would be hard to fit all the points with a straight line with a $A_{\mathrm{H}}/A_{\mathrm{D}} \geq 0.5$.

The discrepancy in k_{H} at the lowest temperature is almost certainly an experimental artifact. The value of k_{D} for this temperature lies quite well on the Arrhenius line. The deviation of k_{H} is in the opposite direction from that expected if Arrhenius equation failure were due to important tunneling. The error may possibly be due to the attempt to extend the temperature range beyond that consistent with precise rate measurements. The range was limited by the solubility of chloranil and fogging of the optics at the low end, and solvent volatility at the high end, as well as possible other unrecognized factors.

The Arrhenius eq 3 has been presented elsewhere,[11] where the imaginary frequency of the equivalent one-dimensional truncated parabolic barrier was estimated at 1150 cm^{-1}, corresponding to a tunnel correction of about 3 on the isotope effect. The importance of tunneling was there also shown by the relatively small size of the tritium isotope effect.

In work on proton transfers, the existence of a large tunnel correction was in one case associated with sterically crowded transition state.[12] Since the most reasonable structure for the transition state for the leuco dye oxidation is also hindered, we have searched for a steric influence on these isotope effects also. The *o*-methoxy substituent was tried for this purpose, and tetrabromoparabenzoquinone was also used. The effect of the *o*-methoxy group is not impressive in any way, nor is there much evidence for steric retardation. The compound reacts slightly more slowly than malachite green with chloranil, slightly more rapidly with bromanil. Thus, there is no really sharp deviation from the expected rate as there was in the case of the proton transfer between hindered pyridines and 2-nitropropanes. Nevertheless, a small increase in the isotope effect appears in each case on going from the unsubstituted compound to the *o*-methoxy substituent and on going from chloranil to bromanil. The rates with iodanil and dichlorodifluoroquinone (Table IV) are not certain enough to warrant interpretation, although they were studied to extend the range of steric variation. The partial substitution of bromine for chlorine also introduces a small and possibly significant increase in isotope effect which might be partly steric in origin but is too small for interpretation. The insensitivity of the isotope effect to substitution in the leuco dye is in agreement with a postulation of Swain[13] for hydride transfer reactions.

The substituent effects on the rates of oxidation in acetonitrile are in reasonable agreement with the earlier work in methanol.[7] Thus *m''*-chloro leuco malachite green **1c** reacts 0.52 times as fast as the unsubstituted compound **1d**; the work in methanol gave a ratio of 0.51. The value of ρ in methanol of -0.81 based upon 4 points can then be accepted as roughly applicable to the new solvent. As described earlier,[7] this corresponds to a rather reagent-like transition state.

It is of interest to see if a linear free-energy relationship is applicable to substitution in both components. Unfortunately, the obvious correlation is with the oxidation potential of the quinones but these are highly solvent dependent,[14] and data in acetonitrile solution are not available. There are polarographic data on some quinone reductions in acetonitrile,[15] and we have chosen to consider the half-wave potential for the first step of the reduction, which is almost certainly represented by eq 5, on the grounds that it does not involve problems

$$Q + e^{-} \longrightarrow Q^{-} \tag{5}$$

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(11) E. S. Lewis and J. K. Robinson, *J. Amer. Chem. Soc.*, **90**, 4337 (1968).

(12) E. S. Lewis and L. H. Funderburk, *ibid.*, **89**, 2322 (1967).

(13) C. G. Swain, R. A. Wiles, and R. F. W. Burden, *ibid.*, **83**, 1945 (1961).

(14) J. B. Conant and L. F. Fieser, *ibid.*, **45**, 2194 (1923); **46**, 1858 (1924); D. E. Kvalnes, *ibid.*, **56**, 667, 2487 (1934).

(15) M. E. Peover, *J. Chem. Soc.*, 4540 (1962).

of protonation which beset the second wave. This is obviously not the ideal model for this purpose, but it perhaps is as justifiable as any other. Figure 2 shows the plot of some of the data of Table IV, only a few points of which are without some problems. In particular, the kinetics are entirely satisfactory only for points 2 and 3, and only a lower limit is available for point 7. A half-wave potential was not available for point 4, *o*-chloranil; it was estimated by assuming that the half-wave potential in acetonitrile differed as much from the oxidation potential in water as do the corresponding potentials of the *para* isomer. For points 5 and 6, the potential is that for unsubstituted diphenoquinone.

It is clearly inappropriate to draw a line through these points, and much better linear free-energy relations with quinones have been obtained,[16] but it is nevertheless clear that the more powerful oxidizing agents react more rapidly showing that some of the product energy is reflected in the transition state energy. This is consistent with the value of ρ for the oxidation by chloranil, which suggests that the transition state is about a quarter to a third of the way along the reaction for coordinate.[7] Clearly a much smaller value of ρ would suggest a much more reagent-like transition state. With this aspect in mind, an attempt was made to study the value of ρ in the oxidation of substituted leuco malachite green by dicyanodichloroquinone. As mentioned above, the rates were too fast to measure, but a competitive method was used to measure the relative rates of oxidation of leuco crystal violet **1a**, L = H, and 4'' nitromalachite green **1e**, L = H. With the observation that these relative rates are a factor of 31.9, we can estimate the value of ρ. We have chosen a value of σ for the p-$(CH_3)_2N$ substituent to fit the Hammett equation for the chloranil oxidation ($\sigma = -0.97$) which then gives a reaction constant ($\rho \sim -0.86$), which is probably not significantly different from the value with chloranil ($\rho = -0.81$). We may conclude that the transition state has about the same amount of product-like character with either quinone. The smaller isotope effect ($k_H/k_D = 7$ for dichlorodicyanoquinone, 11 for chloranil) should therefore not be attributed to a "symmetry" effect on the zero-point energy change derived from real vibrations in the transition state.[17]

We may attribute the faster rate with chlorodicyanoquinone to a markedly reduced activation energy, and then, if we interpret both the very small A_H/A_D and the deviation[11] from the Swain equation as a demonstration of an important tunnel correction with chloranil, it is reasonable to conclude that this tunnel correction should be much reduced with a substantially lower barrier, even if the barrier curvature is unaltered.[18] Thus, the reduced isotope effect is to be expected. Qualitatively, the result is entirely compatible with a tunneling explanation for the large isotope effects and the small A_H/A_D factors with chloranil. Unfortunately, the absence of rates with this highly reactive quinone prevents a more quantitative treatment. It is possible that the different steric requirements of *o*-chloranil are responsible for a decrease in the amount of tunneling and hence the lower isotope effect, but rate uncertainties make this now undemonstrable.

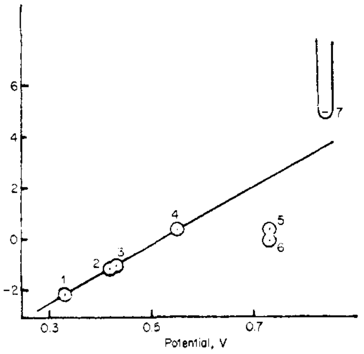

Figure 2. Rough linear free-energy relationships between rates of oxidation of leuco crystal violet by quinones and the first polarographic half-wave potentials of the quinones in acetonitrile. Point identification: 1, 2,5-dichloro-*p*-benzoquinone; 2, bromanil **2b**; 3, chloranil **2a**; 4, *o*-chloranil; 5, tetrachlorodiphenoquinone; 6, tetrabromodiphenoquinone; 7, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone **2f** showing only lower limit for the rate constant.

Experimental Section

Materials. Leuco Crystal Violet 1a, L = H. Crystal violet (**3**, X = p-$N(CH_3)_2$) (8.5 g, biological stain grade) was dried at 150° for 3 hr, and made into a slurry with tetrahydrofuran (900 ml) and placed in a dropping funnel. Lithium aluminum hydride (1.2 g) was weighed out, then about 0.1 of it was added to a 2-l. 3-necked flask containing tetrahydrofuran (100 ml). Then the slurry of dye was added with stirring until a permanent color was produced, then another small portion of lithium aluminum hydride was added, and then dye and hydride alternately until all of both were added. After stirring overnight, the solvent was removed under vacuum and the resulting mixture was taken up in ether (1 l.) and washed with water until the washes were clear. The ether was then removed and the residue crystallized from ethanol giving 5 g (66%) of leuco crystal violet, mp 177–178°. Similarly, reduction of dye with lithium aluminum deuteride gave **1a**, L = D.

The same procedure was used to prepare the *m*-methoxy leuco malachite green-*d* **1b**, L = D, from the dye fluoroborate, which was in turn prepared by the oxidation of the ordinary leuco dye **1b**, L = H, with chloranil.[7] It melted at 147–149°.

The other leuco dyes (**1b**, **1c**, **1d**, and **1e**), L = H, were prepared as before[7] by the condensation of dimethylaniline with the appropriately substituted benzaldehydes.[19] The deuterated benzaldehydes for preparing **1c** and **1d**, L = D, were prepared following Wiberg and Stewart,[20] *via* the reduction of benzil with lithium aluminum deuteride and cleavage with lead tetraacetate. Neither of these routes to deuterated leuco dyes was suitable for **1e**, L = D, and we did not prepare this compound.

The compounds **1**, L = D, prepared by deuteride reduction of the dye did not contain any detectable protium compound contamination, but those prepared from deuterated benzaldehydes contained a per cent or two of protiated compound, as determined by the kinetic analysis. This contamination appeared to be in the benzaldehyde.

Chloranil **2a** (tetrachloro-*p*-benzoquinone) was Eastman practical grade, recrystallized best from ethyl acetate. All quinones, which melt at very high temperatures and sublime, were characterized most easily by the infrared spectrum. The chloranil used had mp 290° (sealed tube).

Dihydrochloranil, used for an authentic sample for the uv absorption, was prepared following the literature,[21] mp 238–240° (sealed tube), reported[21] 230–232°.

Bromanil **2b** (tetrabromo-*p*-benzoquinone), was K & K Lab material purified to a pure yellow color by sublimation and re-

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(16) O. Dimroth, *Angew. Chem.*, **46**, 571 (1933).

(17) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961); L. Melander, ref 9, pp 24–30.

(18) See, for example, R. P. Bell, *Trans. Faraday Soc.*, **55**, 1 (1959), in which the dependence of the tunnel correction on the barrier height shows up as a significant but often neglected term.

(19) The procedure described is not highly satisfactory. An improved procedure, which we used only a few times, appears to be that of R. Cigen, *Acta Chem. Scand.*, **15**, 1905 (1961).

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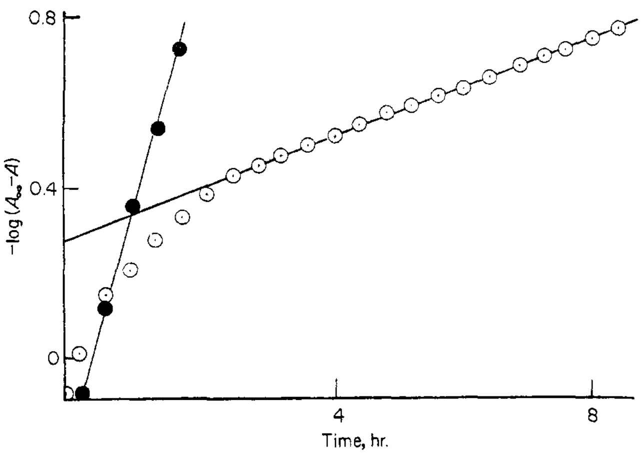

Figure 3. Course of reaction in oxidation of partially deuterated leuco crystal violet (**1a**, L = H + **1a**, L = D) with excess chloranil. Open circles, values of $A_\infty - A$ experimentally observed. Filled circles, calculated course of oxidation of **1a**, L = H, alone, using extrapolation shown to eliminate contribution of the deuterated material; drawn to same scale, but with different origin.

crystallization from ethyl acetate, plates, mp 300°, sealed tube. It was also synthesized from hydroquinone[22] to give an indistinguishable material.

Iodanil **2c** (tetraiodo-*p*-benzoquinone) was prepared from bromanil[23] as black needles, mp 278–279° (sealed tube), reported[23] mp 282–284°.

2,3-Dichloro-5,6-dicyano-*p*-benzoquinone **2h** was recrystallized from chloroform from an Aldrich Chemical Co. sample.

Tetrachloro-*o*-benzoquinone was obtained from Aldrich Chemical Co. and used without purification.

The dibromodichloroquinones (**2d**, **e**, and f) were prepared by bromination of the appropriate dichloroquinones in hot acetic acid.[24] They all melt at approximately the same temperature (295°) and the corresponding hydroquinones also have similar melting points (~235°) and uv spectra. They can be characterized by the ir spectra, however. The dichloroquinones were available by known methods: 2,6-dichloro-*p*-benzoquinone was available from Eastman, 2,5-dichloro-*p*-benzoquinone was prepared by the nitric acid oxidation of the hydroquinone,[25] 2,3-dichloroquinone was prepared following Conant and Fieser,[26] although the procedure was rather sensitive to conditions and occasionally gave the 2,5 isomer.

Dichloro-*p*-xyloquinone (mp 149–150°) was prepared by a modification of the method of Carstanjen.[27] The modification consisted in adding potassium chlorate to the initial brown reaction mixture to complete the oxidation.

The method of Fieser and Martin[28] was used to prepare 2,5-dichloro-3,6-diacetamidoquinone.

Diphenoquinone was prepared in the "gold" form only,[29] and quick drying was essential.

The tetrabromo- and tetrachlorodiphenoquinones were prepared by adding the halogen to *p*,*p*′-biphenol in hot acetic acid, and oxidizing the hydroquinone with nitric acid.[30] Tetrachlorodiphenoquinone appeared as very small orange-red crystals from acetonitrile; the bromo compound was a purplish red powder.

The synthesis of 2,5-dichloro-3,6-difluoroquinone (**2g**) was attempted following the literature procedure by the treatment of chloranil with potassium fluoride.[31] Although the melting point of sublimed fractions was constant, suggesting that the substance obtained was homogeneous, there was substantial uncertainty about the structure of this substance. On hydrolysis with aqueous sodium hydroxide it gave an ultraviolet spectrum consistent with the formation of a 74% yield of chloranilinic acid (λ_{max} 525 nm, $\epsilon = 6.2 \times 10^4$ in 50% aqueous acetonitrile). However, it had mp (sealed tube) 205°, in disagreement with that reported of 213–215°,[31] but in agreement with that reported for a material of questioned identity.[32] The analytical data were inconclusive, presumably because of analytical problems, and were inconsistent with any tetrahaloquinone.

Acetonitrile from a number of sources was used, all of which were equivalent kinetically. The cheapest was Matheson Coleman and Bell practical grade distilled from phosphorus pentoxide. All grades gradually developed an ultraviolet absorption near 260 nm resembling that of benzene. It was probably the trimer, sym-trimethyltriazene.

Methanol was a commercial reagent grade material.

Kinetics. Rates in methanol were initial rates carried only to a few per cent conversion essentially as described before.[7]

Rates in acetonitrile were followed by the appearance of the dye absorption with time and followed to at least two half-lives. The complete ultraviolet spectrum of the solution of leuco crystal violet for the oxidation with chloranil was taken from time to time and shown to be consistent with reaction 1, and this is a rigorous test for side reactions since all the compounds in reaction 1 have strong ultraviolet absorption.

A typical procedure is the following: about 10^{-3} mol of quinone was placed in a 100-ml volumetric flask, 50 ml of solvent was added, and the solution was warmed to effect solution, the flask was filled somewhat short of the mark and 2.3 ml of glacial acetic acid was added and then the flask was placed in the thermostat used to control the cell temperature. It was diluted to the mark after coming to temperature. A stream of nitrogen was passed through the solution for about 5 min to remove oxygen. The solvent loss due to evaporation and the solution loss on the nitrogen inlet tube amounted to less than 1%; they were treated as loss of pure solvent.

Similarly, a 10^{-4} *M* solution of the leuco dye was made up, although the concentration was not usually critical.

A clean, dry, stoppered flask was also placed in the thermostat, a measured volume of the quinone solution was placed in the flask, and another sample was transferred to a 0.1-cm spectrophotometric cell and the spectrum was measured, the cell was cleaned and dried and restored to the sample compartment to come to temperature again. The uv spectrum of the other solution was then taken and the cell was prepared as before. Finally, a sample of the second solution was added to the mixing flask along with the quinone solution, the solutions were mixed rapidly by swirling (or by passing nitrogen through them), and a portion was added to the spectrophotometer cell. After reaching the equilibrium temperature, the measurement of absorbance *vs.* time (at the dye absorption maximum) was made, and the pseudo-first-order rate constant measured as the slope of a plot of ln $(A_\infty - A)$ *vs.* time. In some slow reactions the Guggenheim method was used when A_∞ was not experimentally accessible, and in a few cases, with slightly soluble quinones, A_∞ was estimated from the amount of leuco dye used.

Cell temperatures were assumed to be the same as those ultimately reached by a larger 10-cm cell filled with water. These were measured with a thermistor and related with this instrument to the thermostat temperature. Both the cell compartment and the cell holder were tempered by circulating water from the thermostat. The thermostat temperatures were in turn measured with a mercury thermometer with a U.S. Bureau of Standards calibration. The time constants for approach to constant temperature could be estimated by deviations from the kinetics and no deviations could be detected after about 3 min. These deviations could be minimized when necessary by making sure that the cell and the solutions were very nearly at the final temperature on mixing.

Figure 3 shows a kinetic plot used for deuterium analysis. The initial curved section shows the fall in rate due to consumption of the protiated material, the extrapolation of the linear portion to $t = 0$ gives the absorbance due to the initial deuterium content, and the extrapolation of the observed curve to $t = 0$ (over a very short time) gives the absorbance due to both species together. It is possible to get both k_H and k_D from such a plot, but this was only done to confirm the source of the curvature. The plot also illustrates why the values of k_D need not be corrected for a small contamination of the deuterated leuco dye by protiated material.

The competitive isotope effects with the dicyanodichloroquinone

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were based upon this analysis. A flask with a crease in the bottom which made two separate compartments was used, the quinone solution being placed in one compartment and the leuco dye mixture in the other. The solutions could then be mixed very rapidly by shaking the flask, after it had reached a constant temperature. The rapid mixing is quite necessary and a preliminary isotope effect of 1.5 was measured before the fast mixing technique was used. The two independent determinations of the isotope effect described in the Results Section were done to show that mixing rate problems had been overcome. The successful determination of relative rates in excess of a factor of 30, together with the unlikelihood that that factor could be higher, suggests that the isotope effect is reliable.

Dependence of the Primary Isotope Effect (k^H/k^D) on Base Strength for the Primary Amine Catalyzed Ionization of Nitroethane

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Abstract: Primary kinetic isotope effects (k^H/k^D) have been determined in both water and 50% dioxane–water (v/v) for the primary amine catalyzed ionization of nitroethane and nitroethane-1-d_2. In water the pK_a of nitroethane is 8.5 and the values of k^H/k^D appear to be maximal for amines whose conjugate acids possess pK_a values near 8.5 (*i.e.*, near $\Delta pK_a = 0$). In the 50% dioxane–water solvent the pK_a of nitroethane is 10.7 and it would appear as though the maximum in k^H/k^D, if any, must pertain to amines of pK_a > 10. If one concludes that these results are not fortuitous then it follows that transition state symmetry is dependent upon ground-state basicity. Also, since the Brønsted plots for both k^H and k^D are linear one would be forced to conclude that the primary kinetic isotope effects are a more sensitive probe of transition state than are Brønsted plots.

Theoretical calculations[2] have indicated that the primary deuterium isotope effect (k^H/k^D) for the base (B:) catalyzed ionization of an acid (HA) should reach a maximum value when the difference in basicity of B: and A: (ΔpK) is small. Until recently experimental support of theory has been lacking.[3] This study deals with the determination of k^H/k^D in the region of $\Delta pK = 0$ for the primary amine catalyzed ionization of nitroethane. Our objective has been to ascertain if a maximum in the primary isotope effect occurs and the sensitivity of the primary isotope effect to changes in the acidity of nitroethane due to change in solvent.[4] The relative usefulness of k^H/k^D and the Brønsted coefficient β in determining the position of the transition state along the reaction coordinate is considered.[5]

$$\Delta pK = pK(\mathrm{HA}) - pK(\mathrm{BH}) \qquad (1)$$

Experimental Section

Apparatus. Kinetic measurements were made with a Gilford Model 2000 or a Zeiss PMQ II spectrophotometer. The Zeiss was equipped with a thermostated brass cuvette holder and the Gilford with dual thermospacers through which water was circulated at 30 ± 0.1°. Readings were recorded automatically with either a Honeywell or Servo Riter II recorder.

The pH's of the kinetic solutions were determined both prior to and at the completion of reactions, using a Radiometer Model 22 pH meter with a PHA 630 scale expander, and a combined glass calomel electrode (Radiometer G.K. 2021 C) thermostated at the temperature of each kinetic experiment.

Mass spectra were recorded on an AEI MS 902 mass spectrometer. All pmr spectra were taken neat (TMS as an internal standard) on a Varian HA 100 or a Jeolco C-60HL. A Loenco Model 15C-E vpc with a 16-ft 20M Carbowax column on 60–80 Chromosorb W was used for preparative collection of nitroethane-1-d_2. All calculations were performed on an Olivetti–Underwood Programma 101, and best least squares fit of points was used in plots of k_{obsd} *vs.* B_T. A microliter pipet (Ependorf) was used to deliver stock solutions of substrate and iodine.

Materials. Pyridine (Baker), piperidine (Matheson Coleman and Bell), and 1,2-diaminopropane were distilled from barium oxide, bp 116, 103, and 117°, respectively. Glycylglycine (Aldrich) and hydrochlorides of glycine ethyl ester (Eastman), 2,2,2-trifluoroethylamine (Pierce), ethylamine (Matheson Coleman and Bell), ethylenediamine (Eastman), and ammonia were recrystallized from ethanol-water mixtures and dried under vacuum over phosphorus pentoxide. Tris(hydroxymethyl)aminomethane (Matheson Coleman and Bell) and glycine (Fischer reagent) were used without further purification. Nitroethane (Aldrich) was distilled twice through a 9-in. Vigreux column, bp 113°. Deuterium oxide (Stohler Isotopes, 99.8% isotopically pure) was used without further purification. Spectral grade dioxane (Matheson Coleman and Bell) was refluxed over sodium metal and distilled under nitrogen through a 6-ft vacuum-jacketed column with glass helices (bp 102°) prior to each kinetic run. The resulting dioxane was tested for the presence of peroxides with potassium iodide paper, and with iodine with an excess of iodide by observing changes in absorption at 351 nm. Any solutions containing peroxides were discarded. All solutions containing dioxane were checked for the presence of peroxides prior to and at the completion of each kinetic run.

pK_a Determination. The pK_a of nitroethane in 50:50 (v/v) dioxane-water (μ = 0.2 with KCl at 30°) was determined by half-neutralization and serial dilution. The pK_a values for glycine, glycylglycine, 1,2-diaminopropane, tris, and 2,2,2-trifluoroethyl-

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(1) (a) A portion of the material to be submitted by J. E. D. in fulfillment of the requirement for the Ph.D. in Chemistry, University of California at Santa Barbara. (b) To whom inquiries should be addressed.

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