relatively difficult such that reaction with the original hydrogen is possible. In the benzyl anion–lithium cation case rotation around the primary CH_2 would render internal return with the original hydrogen less probable. A corollary of this rationalization is that loss of configuration is expected to be greater for toluene than the 18% racemization found previously in exchange of optically active ethylbenzene-α-d with LiCHA.[18] We see no practical way of testing this prediction, but the second corollary, that triarylmethanes show *less* racemization, is subject to experimental test.

Finally, these derived a^L values may be combined with the experimental isotope effects to produce the mechanistic isotope effects, $k_I^L/k_I^{L'}$; that is, the isotope effects for the proton transfer step itself. These values are summarized in Table III. The primary isotope effect, k_I^H/k_I^D, of about 11 is high for proton transfer reactions and suggests not only complete loss at the transition state of C–H stretching zero-point energy but that of some C–H bending zero-point energy as well. In the absence of a significant equilibrium isotope effect these values also apply to $k_{-I}^L/k_{-I}^{L'}$. Our entire analysis makes no allowance for tunneling. It is also surely noteworthy that the mechanistic isotope effects for toluene and for triphenylmethane are so similar in magnitude. This correspondence implies a similarity in transition-state structures despite a 10 pK-unit difference in equilibrium ion pair acidity. This further suggests that this equilibrium acidity difference is not fully manifest at the transition state and provides further evidence that the transition state in these reactions is highly pyramidal.[6]

Table III. Derived Isotope Effects at 25°

	k_I^D/k_I^T	k_I^H/k_I^T	k_I^H/k_I^D
Toluene	2.86	32	11
Triphenylmethane	2.90	30–36	10–12

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Acidity of Hydrocarbons. XLVIII. Kinetic Acidities of Mono-, Di-, and Triarylmethanes toward Lithium Cyclohexylamide[1]

A. Streitwieser, Jr.,* M. R. Granger, F. Mares, and R. A. Wolf[2]

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received August 29, 1972*

Abstract: Tritium exchange rates with lithium cyclohexylamide in cyclohexylamine have been determined for several aryl- and polyarylmethanes. Relative rates at 25° are p-biphenylyldiphenylmethane (BDM), 2.3; di-p-biphenylylmethane (DBM), 1.39; triphenylmethane (TPM), 1; diphenylmethane (DPM), 0.28; p-methylbiphenyl (pMB), 0.0048; m-methylbiphenyl (mMB), 0.0021; toluene (Tol), 0.00104. Comparison with known pK values for some of these hydrocarbons gives a linear Brønsted correlation with $\alpha = 0.314$ and permits extrapolation to a pK value for toluene of 40.9. These results indicate that delocalization effects are only partially developed at the transition state and that the central carbon is still highly pyramidal at the transition state.

As part of our continuing study of equilibrium and kinetic acidities of hydrocarbons and their simple derivatives, we report in this paper a study of hydrogen isotope exchange reactivities toward lithium cyclohexylamide (LiCHA) in cyclohexylamine (CHA) of triphenylmethane (TPM), p-biphenylyldiphenylmethane (BDM), diphenylmethane (DPM), bis(p-biphenylyl)-methane (BBM), and p-methylbiphenyl (MB). Equilibrium acidities of these hydrocarbons toward cesium cyclohexylamide (CsCHA) in CHA have been reported previously.[3,4] The combined results lead to a Brønsted comparison of the LiCHA kinetic acidities with the CsCHA equilibrium acidities and yield several important conclusions.

Experimental Section

Materials. The hydrocarbons are all well-known materials and were prepared by standard methods or purchased. Three general methods were used to introduce deuterium and/or tritium into the α positions: (a) reaction with n-butyllithium and quenching with the appropriate water, (b) preparation of the Grignard reagent from the chloride and quenching, and (c) preparation of the Grignard reagent by treatment of the lithium derivative with anhydrous magnesium bromide in ether followed by quenching.

Materials prepared by method a generally gave high infinity values in the kinetic runs suggesting the presence of substantial nonexchangeable isotope. This was confirmed by oxidation of some samples. Ring protonation was almost but not completely absent with the Grignard reagents. Related findings were reported earlier by Russell[5] in reactions of α-cumylpotassium and have also been discussed previously by us.[6]

Kinetic measurements were carried out with our usual procedures in which solutions of hydrocarbon and LiCHA in CHA were prepared in separate parts of a bifurcated reactor under inert atmo-

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sphere.[7,8] After temperature equilibration, the solutions were mixed and aliquots were delivered by internal nitrogen or argon pressure and quenched with dilute hydrochloric acid. For the relatively fast runs (some runs had half-lives of the order of 1 min) a tape recorder was used to record delivery of the aliquots. Tritium content was measured by liquid scintillation counting. Deuterium content was measured by low voltage mass spectrometry or, in the older runs, by infrared comparison with standard mixtures. Pseudo-first-order rate constants were determined with the LSKIN1 program.[9] Corrections for "back-reaction"[10,11] were applied where appropriate but in most cases the concentrations of hydrocarbon were sufficiently small that such corrections were not significant.

Some runs contained fluorobenzene-*2-d,t*. This compound decomposes with LiCHA with destruction of the base catalyst.[12] However, rates relative to exchange in fluorobenzene could still be obtained. In this connection we point out that the kinetic analysis we used previously for such cases[12] is in error. That analysis made use of a ratio of second-order rate functions which assumes a constancy of the catalyst concentration. Since the catalyst concentration actually changes with time the analytical expression is far more complex. This analysis is now done by computer using the program RELRATE;[13] further details will be published separately.

Results and Discussion

The results of these kinetic studies are summarized in Table I. In those cases for which the formal concentration of LiCHA was determined reliably, the pseudo-first-order rate constants were converted to the k_2 values in Table I. Only monomeric LiCHA is assumed to be catalytically active,[10] and its concentration among the inactive aggregated LiCHA was evaluated using model 2 derived previously.[14] The second-order rate constants for toluene were further confirmed in the previous paper.[7]

The data suffice to put all rates, including that for toluene (Tol), on a consistent basis relative to TPM. In several runs the loss of D from DPM-*d* was compared with loss of T from TPM-*t*. In the preceding paper[7] it was shown that the primary isotope effect for TPM is essentially the same as that for toluene and that internal return is negligible, at least for deuterium and tritium exchange; that is, $k_{\rm D}/k_{\rm T}$ is essentially the same for Tol and for TPM and it is reasonable to expect, therefore, that $k_{\rm D}/k_{\rm T}$ primary isotope effects will be essentially constant for the series. With this assumption a relative rate $k_{\rm T}$(DPM)/$k_{\rm T}$(TPM) is easily deduced. The resulting value, 0.29 ± 0.01, compares well with the result of run K11 in which the deuterium rates were compared directly, $k_{\rm D}$(DPM)/$k_{\rm D}$(TPM) = 0.27 ± 0.01. A less accurate value at 50° is available from runs G7, G8, and G11 for which a comparison of second-order rate constants gives $k_{\rm T}$(DPM)/$k_{\rm T}$(TPM) = 0.29 ± 0.03. We expect the relative rate to be slightly compressed at the higher temperature; hence these relative rates compare well.

Table I. Hydrogen Isotope Exchange Rates with LiCHA in CHA

Run	Compd	$10^3k_1^{\rm T}$, sec^{-1}	$10^3k_1^{\rm D}$, sec^{-1}	c[a]	$k_2^{\rm T}$, M^{-1} sec^{-1}
		25.0°			
G10	TPM	6.8 ± 0.1		0.021	1.91
G13	TPM	6.5 ± 0.1		0.021	1.83
G15	TPM	6.6 ± 0.1		0.022	1.82
G16	TPM	6.2 ± 0.1			
	DPM		5.1 ± 0.1		
G17	TPM	6.7 ± 0.1		0.013	2.22
	DPM		5.4 ± 0.3		
K11[b]	TPM	7.87 ± 0.40	22.9 ± 0.8		
	DPM		6.2 ± 0.1		
G18	BDM	15.0 ± 0.4		0.020	4.23
	DPM		4.6 ± 0.6		
M13[c]	TPM	(0.488 ± 0.030)[d]	(0.513 ± 0.005)[e]		
M15[f]	DBM	(0.680 ± 0.010)[g]	(0.570 ± 0.018)[e]		
		50.0°			
G7[h]	DPM	4.2 ± 0.2		0.010	1.6
G8[h]	DPM	4.9 ± 0.2		0.017	1.5
G11[h]	TPM	14 ± 1		0.010	5.3
W2[i]	mMB	7.69 ± 0.26			
	Tol	4.20 ± 0.05			
W3[i]	pMB	18.7 ± 0.4			
	Tol	4.13 ± 0.14			
W5[i]	mMB	10.1 ± 0.2			
	Tol	5.02 ± 0.16			

[a] Formal concentration of LiCHA. [b] Reference 7. [c] Run contained fluorobenzene-*2-d,t* and 1,3-difluorobenzene-*4-d,t*. [d] From D-exchange results using $k_{\rm D}/k_{\rm T}$ = 2.79 ± 0.08 for TPM and 2.66 ± 0.15 for fluorobenzene-*2-d*. [e] Rate relative to fluorobenzene-*2-d* calculated by RELRATE; details to be published separately. [f] Run contained fluorobenzene-*2-d, t*. [g] Rate relative to fluorobenzene-*2-t* calculated by RELRATE. [h] At 49.9°. [i] Tritiodeprotonation.

A rate for BDM is available from run G18 which gives a second-order rate constant for direct comparison with that for TPM. Second-order rate constants contain a possible error in the effective LiCHA concentration. Despite the use of careful vacuum line technique it is always possible for adventitious moisture to lower the effective catalyst concentration. Nevertheless, Granger's runs (G series) are internally consistent and the desired relative rate, $k_{\rm T}$(BDM)/$k_{\rm T}$(TPM) = 2.2 ± 0.2, should not be far off. A check is available from deuterium exchange of DPM in the same run. Although this compound gave kinetic points with substantial scatter, the ratio, $k_{\rm T}$(BDM)/$k_{\rm D}$(DPM) = 3.3 ± 0.4, converts, using the isotope effect, $k_{\rm D}/k_{\rm T}$ = 2.79 ± 0.08 and the $k_{\rm T}$(DPM)/$k_{\rm T}$(TPM) derived above to $k_{\rm T}$(BDM)/$k_{\rm T}$(TPM) = 2.6 ± 0.3. We adopt the weighted average, 2.3 ± 0.2.

Tritium exchange of BBM was measured in run M15 relative to that of fluorobenzene-*2-t*. Deuterium exchange of TPM was measured independently in run M13 relative to fluorobenzene-*2-d*. The corresponding tritium rate contained a systematic error but is available from the deuterium rate and the ratio of the primary isotope effects. This approach gives $k_{\rm T}$(BBM)/$k_{\rm T}$(TPM) = 1.39 ± 0.09.

TPM is related to toluene *via* the second-order rate constants.[14] These values for TPM are essentially constant for an almost twofold change in the formal LiCHA concentration and give a ratio $k_{\rm T}$(TPM)/$k_{\rm T}$(Tol) = 965 ± 90. The single $k_2^{\rm T}$ value available for TPM at 50° allows the derivation of the activation

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parameters, $\Delta H^{\ddagger} = 7.1$ kcal/mol, $\Delta S^{\ddagger} = -33$ eu. The values previously determined for D exchange of toluene are $\Delta H^{\ddagger} = 8.8$ kcal/mol, $\Delta S^{\ddagger} = -39$ eu;[14] correcting for the isotope effect,[7] these values become for T exchange, $\Delta H^{\ddagger} = 9.5$ kcal/mol, $\Delta S^{\ddagger} = -39$ eu.

The methylbiphenyl runs contained toluene so that relative rates are derived directly. These runs were carried out in CHA-*t*. The rates of incorporation of T are equivalent to k_T except that corrections are necessary for the incorporation of tritium into the aromatic rings; benzene hydrogens are known to be 0.01 as reactive as the benzylic hydrogens of toluene.[8] The correction was made by taking several infinity points at long times and extrapolating back. However, this correction only amounted to a few per cent.

The relative rates are summarized in Table II. The methylbiphenyl runs are at 50° and the relative rates were extrapolated to 25° assuming that the entire effect is in the activation energy. Relative equilibrium acidities are available for five of these hydrocarbons toward CsCHA in CHA (Table II). A plot of these quantities gives the linear Brønsted relation in Figure 1 in which the slope, $\alpha = 0.31$, is a relatively low value. This relatively low value has some important implications.

Table II. Relative Tritium Exchange Rates with LiCHA

Compd	Rel rate 25°	p*K*
BDM	2.3 ± 0.2	30.2
DBM	1.39 ± 0.09	30.83
TPM	1	31.45
DPM	0.28 ± 0.01	33.38
pMB[a]	0.0048 ± 0.0006	38.73
mMB[b]	0.0021 ± 0.0002	(39.95)[c]
Tol	0.00104 ± 0.00010	(40.91)[c]

[a] $k_T(\text{pMB})/k_T(\text{Tol}) = 4.1 \pm 0.4$ at 50°. [b] $k_T(\text{mMb})/k_T(\text{Tol}) = 1.91 \pm 0.08$ at 50°. [c] Extrapolated from Figure 1.

The conjugate bases of these hydrocarbons are relatively stable carbanions whose stabilization is derived largely by charge delocalization. The low α value implies that such conjugative stabilization is relatively undeveloped at the transition state. Yet the comparatively high primary isotope effects ($k_H/k_D = 11$)[7] strongly suggest that the original C–H bond is essentially broken at the transition state; *e.g.*, the transition state is "symmetrical" in terms of bonding to H. The logical conclusion of these propositions is that the central carbon is still substantially pyramidal at the transition state; this carbon is highly carbanionic in nature but only a portion of this charge can delocalize. Inherent in this argument is the valuable premise that for highly conjugated systems in which the principal mechanism of ionic stabilization is charge delocalization, the Brønsted α is reliable criterion of the degree of such delocalization. As such, this use of α differs completely from that in which an important mechanism of ionic stabilization comes from charge–dipole electrostatic interactions. It is now well known that the difference in charge distributions in the transition state and in the equilibrium anion in the latter cases can give a variety of α values, including values greater than unity.[15–17]

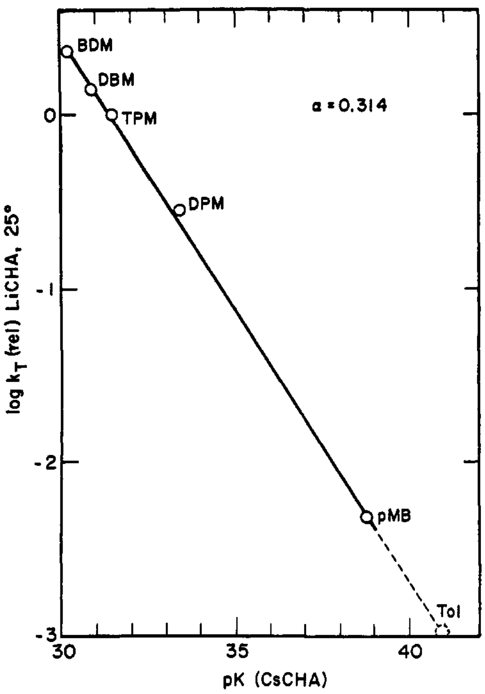

Figure 1. Brønsted correlation of arylmethanes between tritium exchange rates with LiCHA and p*K*'s based on equilibria of cesium salts in CHA.

A highly pyramidal transition state in which delocalization effects are only partially developed more readily allows for the relative constancy of transition-state structure implied by a linear Brønsted plot over an extended p*K* range. The equilibrium p*K* of a planar system is only a partial determinant of the p*K* of the transition-state configuration. The present interpretation also makes understandable the near identity of the primary isotope effects for the proton transfer step of both toluene and triphenylmethane,[7] whose equilibrium ion pair p*K*'s differ by 10 units (*vide infra*).

The new hypothesis also explains some hitherto puzzling features of the exchange rates of substituted toluenes with LiCHA; these rates followed a $\sigma\rho$ correlation with indication of comparatively little charge delocalization into the rings;[18] for example, the derived value of ρ for reaction of toluenes, 4.0, is comparable to that for the exchange of bridgehead hydrogens in substituted triptycenes with CsCHA,[19] in which conjugation with the aryl rings is impossible. We conclude also that the secondary deuterium isotope effect measured previously[20] by exchange of $C_6H_5CD_3$ results more from an "inductive effect" of deuterium[21,22] than from a change in hybridization of an α-C–H bond.

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These same conclusions undoubtedly apply also to the deuterium exchange of similar hydrocarbons with lithium *N*-methylanilide reported by Ebel and Ritterbusch.[23] The reactivity ratio of DPM to TPM, 0.59 at 150°, shows a smaller effect of structure than does the exchange with LiCHA. Similarly, ring methyl substitution corresponds to a normal ρ value; yet, the primary isotope effect is large. The extensive experimental results of Ebel and Ritterbusch are readily interpretable in terms of a largely pyramidal transition state.

The present hypothesis of a highly pyramidal transition state for a proton transfer reaction leading to a delocalized carbanion differs from certain assumptions currently made in organic reaction mechanism theory. An important implication of our interpretation is that in this system the measure of the extent of reaction along the reaction coordinate differs for different reaction coordinates. The extent of reaction at the transition state as measured by the leaving proton is different from that measured by the deviation from planarity of the central carbon or the degree of charge transfer into the π system. Consequently, for such a system the extended Hammett postulate[24] does not apply.

Cyclohexylamide anion, however, is a strong base (cyclohexylamine is estimated to have a pK_a in the high 30's relative to CsCHA), and for such a system it is perhaps less difficult to accept that structural reorganization leading to a planar carbanion could lag behind proton transfer. Nevertheless, this type of result appears increasingly to be general for all proton transfer reactions in which proton transfer is accompanied by substantial molecular reorganization as in the general case of carbon acids whose conjugate bases are delocalized.

A further characteristic of such systems appears to be Brønsted correlations that are linear over long p*K* ranges, although the members of the Brønsted family must be chosen carefully.[25] Isotopic exchange reactions of fluorene-type hydrocarbons with methanolic NaOMe have a relatively small Brønsted α.[25] The extensive work of Bordwell with proton transfer reactions of nitroalkanes is also strongly indicative of a highly pyramidal transition state.[26]

Figure 1 shows that the present case is one for which the Brønsted correlation is accurately linear over an extended range. This plot was established using the experimental rate constants for tritium exchange. Such experimental rates have been established to be close to the rates for the primary tritium-transfer step for both toluene and TPM;[7] that is, internal return complications are minimized with the tritium isotope in this system and the observed linear correlation in Figure 1 has theoretical significance. Although care must generally be taken in interpreting relative kinetic acidities in terms of corresponding equilibrium acidities, the present case is that of a Brønsted family in which one principal mechanism of ion stabilization—charge delocalization—is dominant, and the comparison of the two acidities is justified. One should be wary in extending this comparison to systems with heteroatom substituents. Nevertheless, the present Brønsted correlation permits some important extensions, the most notable of which is the rather short extrapolation to give a p*K* value of 40.9 for toluene (per hydrogen). The acidity of this fundamental hydrocarbon has been inadequately studied in the past and had not been well established. It forms a key role in Cram's MSAD scale, for example.[27] The value of 35 assigned as the p*K* of toluene in that scale is considerably less than that given by our results. Despite the importance of the p*K* of toluene, it has never been measured in any direct manner and the usually quoted p*K* is actually the result of some rather crude measurements of McEwen[28] 3.5 decades ago. The present assignment is undoubtedly the most reliable p*K* value available for toluene, subject to the usual limitations of such p*K* values. That is, these values actually refer to equilibrium ion pair acidities of cesium carbanide ion pairs in CHA (eq 1); the p*K*'s are based on the value 18.49 as the approximate p*K* of 9-phenylfluorene with the dilute aqueous solution as standard state and the assumption that relative CsCHA ion pair acidities are the same as relative ionic aqueous acidities.

$$R^-Cs^+ + R'H \overset{K}{\rightleftharpoons} RH + R'^-Cs^+ \tag{1}$$

Kinetic acidities of methylarenes with LiCHA were reported some time ago.[29] These compounds are so similar in structure to toluene and pMB that the same Brønsted correlation surely applies. The relative rates for deuterium exchange are converted to the corresponding p*K* values in Table III. The methylarene results were all determined at 49.9–50.0°. Consequently, the Brønsted slope was adjusted to put the entire effect into the enthalpy of activation; that is, for Table III an effective value of α of 0.289 was assumed compared with the value of 0.314 shown in Figure 1 for 25°. Once again we emphasize that the p*K* differences between related compounds have greater significance than the absolute values but that the absolute values given are the best available at the present time. Note that the

Table III. Kinetic and Equilibrium Acidities of Methylarenes

$ArCH_2$–, Ar =	Rel rate D exchange LiCHA, 49.9°	pK^a
Phenyl	1	(40.9)
1-Naphthyl	10.3	37.4
2-Naphthyl	7.4	37.9
3-Phenanthryl	14	37.0
9-Phenanthryl	19	36.5
2-Anthracenyl	31	35.8
1-Pyrenyl	190	33.0
2-Pyrenyl	15	36.9
4-Pyrenyl	40	35.4
3-Fluoranthyl	200	33.0
8-Fluoranthyl	14	37.0

[a] Derived from the relative exchange rates for p*K*(toluene) = 40.91 and Brønsted α = 0.289. Values are given on a per-hydrogen basis.

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derived pK values for the higher polycyclic methylarenes are down in the polyarylmethane region and should be amenable to direct equilibrium measurement. Unfortunately, with CsCHA the higher polycyclic benzenoid hydrocarbons rapidly form radical anions such that we have been unable to accomplish such direct measurement.

The present pK results may be related to the exchange rates of Ebel and Ritterbusch with lithium *N*-methylanilide at 150°.[23] Their relative deuterium exchange rates for TPM, DPM, and 9-methylphenanthrene give a Brønsted α of about 0.26 at 150°, a value that corresponds to ~0.37 at 25° if the effect is all in $\Delta H^{\ddagger}$. Hence, this reaction is much like that with LiCHA except that the anilide ion is a weaker base and higher temperatures are required for equivalent reactivities.

Aromatic Halogenation. IV.[1a] Kinetics and Mechanism of Iodination of Phenol and 2,6-Dibromophenol

Erling Grovenstein, Jr.,* Nazar S. Aprahamian,[1b]
Coleman J. Bryan, N. S. Gnanapragasam, Donald C. Kilby,
John M. McKelvey, Jr., and Robert J. Sullivan

Contribution from the School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332. *Received November 16, 1972*

Abstract: The kinetics of iodination of phenol has been studied at 25.0° in dilute aqueous solutions of perchloric acid. From the observed dependence of rate upon the concentrations of phenol, iodine, iodide ion, and hydrogen ion, a mechanism is proposed wherein at very low iodide ion concentration molecular iodine makes a rate-determining attack upon phenoxide anion to give an intermediate iodocyclohexadienone; at high iodide ion concentration, this intermediate is formed in a reversible reaction and the rate-determining step shifts to deprotonation of the intermediate. This mechanism is confirmed by a similar study upon phenol-*2,4,6-d*$_3$. The isotope effect (k_H/k_D) increased from a value of 3.0 at an iodide ion concentration of 3×10^{-7} M, at which the iodination step is partially rate determining, to a limiting value of 6.2 at high iodide ion concentrations. In acetate buffers at high iodide ion concentration, acetate ion helps deprotonate the intermediate iodocyclohexadienone with an isotope effect which is about the same as that in dilute aqueous perchloric acid. In acetate buffer the isotope effect decreases with decreasing iodide ion concentration; however, the minimum value observed for the isotope effect was 3.4 at 3×10^{-7} M iodide ion rather than a smaller value that obtained in dilute aqueous perchloric acid solution. This unexpected result is explained on the basis of participation of acetyl hypoiodite as an iodinating agent at very low iodide ion concentration. The previously studied kinetics of iodination of adrenochrome may be explained by a mechanism similar to that proposed for phenol. Large isotope effects were observed in iodination and small isotope effects in bromination of 2,6-dibromophenol.

According to previous investigations,[2,3] the iodination of phenol in aqueous solution follows the rate expression

$$\mathrm{d}(\mathrm{I}_2)/\mathrm{d}t = k[\mathrm{PhOH}][\mathrm{I}_2]/[\mathrm{H}^+][\mathrm{I}^-] + k'[\mathrm{PhOH}][\mathrm{I}_2][\mathrm{HA}]/[\mathrm{H}^+]^2[\mathrm{I}^-] \quad (1)$$

where HA is a buffer acid such as acetic acid. Here, as in other sections of this paper, entities enclosed in brackets refer to the actual concentration of the species shown, whereas those in parentheses refer to a stoichiometric concentration, thus the concentration of iodine as determined by thiosulfate titration. On the assumption that attack of the iodinating agent upon the substrate occurs in the rate-determining step, the first term of this equation has been interpreted[2,3] to involve attack of HOI upon un-ionized phenol or, alternatively, of H_2OI^+ or I^+(aq) upon phenoxide ion; the second term to involve a general acid catalyzed attack of HOI or attack of AI (*e.g.*, acetyl hypoiodite) upon phenoxide ion. With the discovery[4] that iodination of phenol-*2,4,6-d*$_3$ occurs considerably more slowly than iodination of ordinary phenol and that, therefore, breaking of the C–H bond of phenol is part of the rate-determining step, it was recognized that the nature of the iodinating agent could not be specified since, very likely, under the kinetic conditions so far investigated, transfer of iodine cation from an iodinating agent to phenol occurs in a rapid, reversible step prior to proton loss.

While experimental verification of the mechanism of iodination of phenol remains at this indefinite stage, a detailed study[5] of the iodination of *p*-nitrophenol has revealed a mechanism in which molecular iodine attacks *p*-nitrophenol or, more readily, *p*-nitrophenoxide ion in a reversible process to give an intermediate which in a second, generally rate-determining step, loses a proton from carbon to yield, after protonation on oxygen, 2-iodo-4-nitrophenol. This mechanism was affirmed both by a kinetic study down to low iodide ion concentrations (2×10^{-5} M), wherein the iodination step itself became partially rate-determining, and by the decrease in the kinetic isotope effect k_H/k_D from 5.4 at 222×10^{-5} M iodide to 2.3 at about 1.5×10^{-5} M iodide.

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(1) (a) Part III: E. Grovenstein, Jr., and F. C. Schmalstieg, *J. Amer. Chem. Soc.*, **89**, 5084 (1967); see also E. Grovenstein, Jr., and E. Helgstrand, *Sv. Kem. Tidskr.*, (4) 31 (1970); (b) deceased June 17, 1972.

(2) B. S. Painter and F. G. Soper, *J. Chem. Soc.*, 342 (1947); F. G. Soper and G. F. Smith, *ibid.*, 2757 (1927).

(3) E. Berliner, *J. Amer. Chem. Soc.*, **73**, 4307 (1951).

(4) E. Grovenstein, Jr., and D. C. Kilby, *ibid.*, **79**, 2972 (1957).

(5) E. Grovenstein, Jr., and N. S. Aprahamian, *ibid.*, **84**, 212 (1962).

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