Relative Reactivities of Methanol and Methoxide Ion as Hydrogen Atom Donors to the p-Nitrophenyl Radical[1]

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Abstract: The relative hydrogen atom donor reactivities of CH_3OH and CH_3O^- toward the p-nitrophenyl radical are measured by the method of *ad eundem* competition. p-Nitrophenyl radical is generated, by the decomposition of methyl p-nitrophenylazo ether, in methanolic $NaOCH_3$ solutions in the presence of iodobenzene or neopentyl iodide, and the ratio of nitrobenzene to p-nitroiodobenzene yields is measured as a function of $NaOCH_3$ concentration. From the data, the hydrogen donor reactivity of CH_3O^- is reckoned to be 45 ± 10 times greater than that of CH_3OH. The data also furnish estimates of the hydrogen donor reactivities of these species relative to the iodine donor reactivities of the iodo compounds used.

Although the relative reactivities of numerous hydrogen atom donors toward reactive radicals have been measured,[2] such measurements appear not to have encompassed conjugate pairs of hydrogen donors comprising an alcohol and the corresponding alkoxide ion.

Most relative reactivity data have been obtained from direct competition experiments. The radical is generated in the presence of the hydrogen atom donor and a standard halogen atom donor (often CCl_4), and the relative rates of hydrogen and halogen atom abstraction are reckoned from the yields of the respective products with attention to the concentrations of the donor species.[3] For example, relative hydrogen donor reactivities toward the phenyl radical were measured by Bridger and Russell[4] and toward the p-nitrophenyl radical by Pryor and coworkers.[5]

The experimental method used in the cited studies[4,5] requires solubility of the hydrogen donor species in CCl_4 or other halogen donor. Although it could be and was applied to study of the hydrogen donor activity of methanol, extension of it to methoxide ion would encounter obvious difficulties. Even if a methoxide salt soluble in CCl_4 could be found, with a cation devoid of hydrogen donor reactivity, interpretation would be complicated by ion association effects. Furthermore, it is in methanol solution that knowledge of the hydrogen donor reactivity of methoxide ion would be most useful. However, direct competition between methoxide ion and a halogen donor in methanol solution would not be feasible because methanol is itself a good hydrogen atom donor.

On the other hand, the problem can be dealt with by the method of *ad eundem* competition.

Method of *ad eundem* Competition.[6] This method is useful when the competing reactions of a reactive intermediate with two species give the same product. To our knowledge, the method was first employed (in another type of system) by Mack and Huisgen.[7a] Also, the use of a similar principle is implied by Pryor and coworkers.[7b] One places the two reactions that give the same product in competition with a third reaction that gives a different product, and then measures the product ratio as a function of reactant concentration ratios.
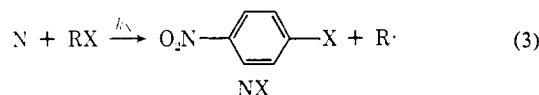
In the case of immediate interest, p-nitrophenyl radical (N) may react with methanol (eq 1) or meth-

$$O_2N\langle\rangle\cdot + CH_3OH \xrightarrow{k_H^0} O_2N-\langle\rangle-H + \cdot CH_2OH \quad (1)$$
$$\quad N \qquad\qquad\qquad\qquad\qquad NH$$
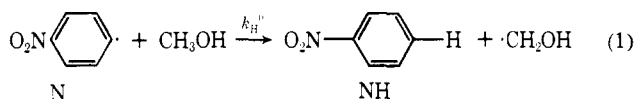
oxide ion (eq 2) to form nitrobenzene (NH). Placed

$$N + CH_3O^- \xrightarrow{k_H^-} NH + \cdot CH_2O^- \quad (2)$$
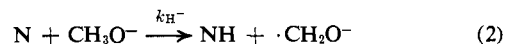
in competition with these two is reaction with a halogen donor $(RX)^5$ to form a p-nitrohalobenzene (NX), as in eq 3.

$$N + RX \xrightarrow{k_X} O_2N-\langle\rangle-X + R\cdot \quad (3)$$
$$\qquad\qquad\qquad\qquad NX$$

Assuming that these reactions are all second order, we write

$$d[NH]/dt = k_H^0[N][CH_3OH] + k_H^-[N][CH_3O^-] \quad (4)$$

$$d[NX]/dt = k_X[N][RX] \quad (5)$$

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. This research was supported in part by the National Science Foundation.

(2) G. A. Russell in "Free Radicals," Vol. I, J. K. Kochi, Ed., Wiley, New York, N. Y., 1973, pp 275-331.

(3) The method of direct competition is discussed by G. A. Russell in "Investigation of Rates and Mechanisms of Reactions," 2nd ed, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience, New York, N. Y., 1961, p 344; L. P. Hammett, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1970, p 91.

(4) R. F. Bridger and G. A. Russell, *J. Amer. Chem. Soc.*, **85**, 3754 (1963).

(5) W. A. Pryor, J. T. Echols, Jr., and K. Smith, *J. Amer. Chem. Soc.*, **88**, 1189 (1966); W. A. Pryor, K. Smith, J. T. Echols, Jr., and D. L. Fuller, *J. Org. Chem.*, **37**, 1753 (1972).

(6) From the Latin *ad eundem fructus*, to the same product.

(7) (a) W. Mack and R. Huisgen, *Chem. Ber.*, **93**, 608 (1960); (b) W. A. Pryor, U. Tonellato, D. L. Fuller, and S. Jumonville, *J. Org. Chem.*, **34**, 2018 (1969).

(8) As a general principle the third, comparison reaction does not have to be halogen atom abstraction. J. A. Zoltewicz and T. M. Oestreich have shown that the 4-isoquinolyl radical in methanolic solutions containing both $NaOCH_3$ and $NaSC_6H_5$ undergoes competing hydrogen abstraction, from CH_3OH and CH_3O^-, and combination with thiophenoxide as a nucleophile. Their observations of the dependence of the isoquinoline/4-thiophenoxyisoquinoline yield ratio on $NaOCH_3$ concentration indicate that methoxide ion is a much better hydrogen atom donor than methanol. Indeed, they formulated an equation equivalent to our eq 6 and constructed a plot of their data analogous to our Figure 1. However, the uncertainties of the slope and intercept were too great to enable evaluation of the CH_3O^-/CH_3OH reactivity ratio; see T. M. Oestreich, Dissertation, University of Florida, 1973; J. A. Zoltewicz and T. M. Oestreich, *J. Amer. Chem. Soc.*, **95**, 6863 (1973).

If the concentrations of CH_3OH, CH_3O^-, and the halogen donor are all much greater than the initial concentration of the radical precursor, $d[NH]/d[NX]$ will equal $[NH]_\infty/[NX]_\infty$, the product ratio at the end of reaction. From division of eq 4 by eq 5, it then follows that

$$\frac{[NH]_\infty}{[NX]_\infty} = \frac{k_H^0[CH_3OH]}{k_X[RX]} + \frac{k_H^-[CH_3O^-]}{k_X[RX]} \quad (6)$$

Equation 6 is conveniently rewritten

$$[NH]_\infty[RX]/[NX]_\infty = (k_H^0/k_X)[CH_3OH] + $$
$$(k_H^-/k_X)[CH_3O^-] \quad (7)$$

This implies that if a series of runs is performed with varying methoxide ion concentration, a plot of the experimental quantity on the left against $[CH_3O^-]$ will be linear, with slope k_H^-/k_X and intercept $(k_H^0/k_X)\cdot[CH_3OH]$. Since the molar concentration of methanol can be calculated, this provides an evaluation of the hydrogen donor reactivities of methoxide ion and methanol vs. the halogen donor. The slope/intercept ratio is $k_H^-/(k_H^0[CH_3OH])$, from which the reactivity of methoxide ion relative to methanol can be reckoned.

Design of the Experiment. As precursor of the p-nitrophenyl radical, we chose methyl p-nitrophenylazo ether. One of its stereoisomers, the trans isomer (t-NE), is a solid compound easily prepared.[9,10a] The

O_2N—⟨benzene ring⟩—N
$\quad$⟍N—OCH_3
t-NE

O_2N—⟨benzene ring⟩—I
NI
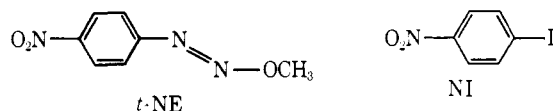
fact that nitrobenzene nearly free of deuterium is obtained from decomposition of t-NE in CH_3OD in the absence of $NaOCH_3$ or containing 2 M $NaOCH_3$[10b] testifies to the intermediacy of p-nitrophenyl radicals, since they abstract hydrogen mainly from the methyl group rather than from the hydroxy group of methanol.[11] That p-nitrophenyl radicals are intermediates is also shown by our observation that p-nitroiodobenzene (NI) is formed in substantial amounts when t-NE decomposes in methanolic $NaOCH_3$ solutions containing iodobenzene; the iodine atom of iodobenzene is abstractable by aryl radicals.[12] The cis isomer of t-NE is an intermediate in its formation from p-nitrobenzenediazonium ion and methoxide ion in methanol,[13] but that will not greatly concern us in the present work.

Inasmuch as the reactivity ratio of principal interest, k_H^-/k_H^0, is obtained from a slope/intercept ratio, it is necessary that the relative error in each be small. The halogen donor must be neither too weak nor too strong.[14] If it is too weak, the relative error in the denominator of each point in the plot of $[NH]_\infty/[NI]_\infty$ vs. $[OCH_3^-]$ will be large. If it is too strong, the same

(9) H. v. Pechmann and L. Frobenius, *Ber.*, **27**, 672 (1894).
(10) (a) J. F. Bunnett and H. Takayama, *J. Org. Chem.*, **33**, 1924 (1968); (b) *J. Amer. Chem. Soc.*, **90**, 5173 (1968).
(11) *Cf.* also E. König, H. Musso, and U.-I. Zahorszky, *Angew. Chem., Int. Ed. Engl.*, **11**, 45 (1972).
(12) (a) J. F. Bunnett and C. C. Wamser, *J. Amer. Chem. Soc.*, **88**, 5534 (1966); (b) D. L. Brydon and J. I. G. Cadogan, *J. Chem. Soc. C*, 819 (1968).
(13) W. J. Boyle, Jr., T. J. Broxton, and J. F. Bunnett, *Chem. Commun.*, 1469 (1971).
(14) CCl_4 was found to be too weak as a halogen donor; no detectable amount of p-nitrochlorobenzene was formed from decomposition of t-NE in methanolic $NaOCH_3$ containing 0.1 M CCl_4.

problem will arise in regard to the numerator for each point. Large relative errors in individual points will cause large relative errors in the slope and intercept.

Further requirements are that the halogen donor be stable under the conditions of the experiment, and that the products NH and NX be stable. We had to reject one otherwise promising halogen donor, bromotrichloromethane, because it reacts with high concentrations of $NaOCH_3$ in methanol as shown by the formation of a white precipitate. p-Nitrohalobenzenes react with methanolic $NaOCH_3$ to form p-nitroanisole (NA),[15] but the reaction is comparatively slow and the complication is easily dealt with by adding the amount of NA to that of NX for calculation purposes.

Two halogen donors were found to be satisfactory for our purposes: iodobenzene[12] and neopentyl iodide. Like the former, the latter is a good iodine atom donor to aryl radicals.[16] Also, its structure forbids E2 or SN2 reactions with $NaOCH_3$ that would complicate the utilization of other alkyl iodides.[17] Of these two, the reactivity of neopentyl iodide is greater and somewhat more suitable for our purposes because of error considerations mentioned above.

Results

We report six series of runs, four with iodobenzene as iodine donor and two with neopentyl iodide. Each series comprises five runs, in which the $NaOCH_3$ concentration is varied from about 0.2 M to about 1.2 M. The yields of nitrobenzene (NH), p-nitroiodobenzene (NI), and p-nitroanisole (NA) obtained in all runs are listed in Table I.

The summed yields of NH, NI, and NA for individual runs total 80–94% for the iodobenzene and 74–93% for the neopentyl iodide runs. In general, the sum of yields is lower at lower $NaOCH_3$ concentrations. Other studies indicate that the methylenimine of p-nitroaniline is formed as a minor product during the decomposition of t-NE in methanol at low $NaOCH_3$ concentrations, and that the dediazotization process which produces it is decreasingly significant as $NaOCH_3$ concentration rises.[19] We did not seek to determine N-(p-nitrophenyl)formaldimine in this work; it is evident that its formation does not disturb NH/NI product ratios.

For each series of experiments in Table I, a plot of $[RI](\% NH)/(\% NI_t)$ vs. $[NaOCH_3]$ was constructed, where $\% NI_t = \% NI + \% NA$. All such plots were linear; the plot for series A, presented as Figure 1, is representative. All the sets of data were subjected to linear regression analysis, and the results are displayed in Table II.

According to the method of *ad eundem* competition (*vide supra*), multiplication of the slope/intercept ratio by the molar concentration of methanol gives k_H^-/k_H^0, the hydrogen donor reactivity of methoxide ion toward p-nitrophenyl radical relative to that of methanol.

(15) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1951).
(16) W. C. Danen and R. L. Winter, *J. Amer. Chem. Soc.*, **93**, 716 (1971).
(17) Neopentyl iodide cannot undergo β elimination. The rate of its SN2 reaction with ethoxide ion in ethanol at 30° is *ca.* 3 × 10^{-9} M^{-1} sec^{-1}, calculated from data of Dostrovsky and Hughes.[18] This corresponds to a half-life of about 7.3 years with 1 M ethoxide.
(18) I. Dostrovsky and E. D. Hughes, *J. Chem. Soc.*, 157 (1946).
(19) H. Hoch and J. F. Bunnett, unpublished observations; it is possible that p-nitroaniline is first formed, and then condenses with the formaldehyde by-product of dediazoniation.
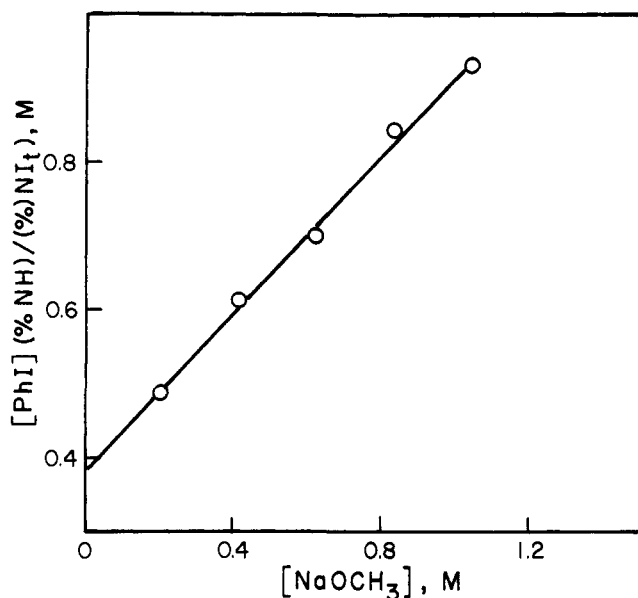
Figure 1. Plot of data from series A, Table I, according to eq 7.

Table I. Yields of Nitrobenzene (NH), p-Nitroiodobenzene (NI) and p-Nitroanisole (NA) from Decomposition of Methyl p-Nitrophenylazo Ether in Methanolic $NaOCH_3$ Solutions Containing Iodine Atom Donor Species[a]

[NaOCH₃], M	NH, %	NI, %	NA, %
Series A; with C₆H₅I, 0.25 M			
0.21	55.1	27.7	0.5
0.42	60.4	24.0	0.6
0.63	64.8	22.2	1.0
0.84	68.0	18.9	1.3
1.05	67.7	16.8	1.6
Series B; with C₆H₅I, 0.25 M			
0.254	54.6	26.1	0.2
0.508	61.0	24.6	0.4
0.762	67.6	20.7	1.0
1.02	75.5	19.3	1.5
1.27	73.2	15.3	2.1
Series C; with C₆H₅I, 0.50 M			
0.254	41.4	41.3	0.3
0.508	47.6	37.4	1.0
0.762	56.1	34.0	1.2
1.02	61.8	30.5	1.9
1.27	63.7	25.9	2.5
Series D; with C₆H₅I, 0.50 M			
0.209	37.9	41.1	0.4
0.418	47.7	38.9	1.3
0.627	51.5	35.0	1.3
0.836	55.2	31.8	1.6
1.05	59.9	29.1	2.3
Series E; with (CH₃)₃CCH₂I, 0.10 M			
0.254	32.0	45.3	0.4
0.508	37.7	42.3	0.6
0.762	45.5	37.1	1.2
1.02	52.0	35.7	1.7
1.27	58.5	31.7	3.1
Series F; with (CH₃)₃CCH₂I, 0.20 M			
0.226	18.3	55.0	0.4
0.452	23.1	52.0	0.7
0.678	28.4	50.4	1.4
0.904	33.8	49.0	2.1
1.13	39.3	46.8	3.2

[a] Temperature, 30.0°; initial concentration of t-NE, 0.01 M.

That result is tabulated for each series of runs in the far right-hand column of Table II. It should be a constant, and it is somewhat disturbing that as measured it varies from about 34 from runs in which iodobenzene was 0.25 M to about 42 when iodobenzene was 0.50 M to about 56 when neopentyl iodide was the halogen donor.

We do not fully understand why these results vary as they do. Appreciable error is of course to be expected in quantities obtained by taking a ratio of ratios of experimental measurements. From experimental error considerations mentioned above, and with attention to the fact that NI yields were relatively low in series A and B, we suspect that the results from those series may be more severely affected by some systematic error than from the other series. The same criticism perhaps applies, but less severely, to series C and D. Possible sources of systematic error are discussed below.

We judge that k_H^-/k_H^0 is best evaluated as 45 ± 10.

With attention to eq 7, one may reckon from the slopes and intercepts of Table II the relative reactivities of CH_3OH and CH_3O^-, as hydrogen donors, vs. iodobenzene and neopentyl iodide as iodine donors. Using the average intercept and slope from series A–D, we calculate k_{MeOH}/k_{PhI} as 1.5×10^{-2} and k_{MeO^-}/k_{PhI} as 0.57, respectively. Likewise, from the average intercept and slope of series D and E, respectively, k_{MeOH}/k_{neoPI} is 1.8×10^{-3} and k_{MeO^-}/k_{neoPI} is 9.9×10^{-2}.

Discussion

From our measurements, we estimate that methoxide ion is 45 ± 10 times as reactive as methanol as a hydrogen atom donor to p-nitrophenyl radical, in methanol solution at 30°.

This result may be compared with the reactivities of several alkanoic acids, relative to their conjugate bases, toward hydrogen atom in water solution.[20] There is evidence that hydrogen atom abstraction occurs, to form H_2.[20] The acetate ion/acetic acid reactivity ratio is reported to be 6.0, and the corresponding ratios for

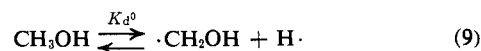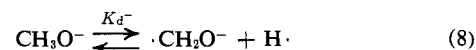(20) P. Neta and R. H. Schuler, *J. Phys. Chem.*, 76, 2673 (1972).

other $RCOO^-/RCOOH$ pairs vary from 1.15 to 3.6, except that the $HCOO^-/HCOOH$ ratio is 176.[20]

Our comparison of kinetic reactivity may be compared with the thermodynamic tendencies of methoxide ion and methanol to dissociate hydrogen *atoms*. The dissociation reactions are

$$CH_3O^- \xrightleftharpoons{K_d^-} \cdot CH_2O^- + H \cdot \qquad (8)$$

$$CH_3OH \xrightleftharpoons{K_d^0} \cdot CH_2OH + H \cdot \qquad (9)$$

Having written the usual expressions for equilibrium constants, we may divide one by the other, to obtain

$$\frac{K_d^-}{k_d^0} = \frac{[\cdot CH_2O^-][CH_3OH]}{[\cdot CH_2OH][CH_3O^-]} \qquad (10)$$

However, the right-hand side of eq 10 is also obtained by dividing the dissociation constant of $\cdot CH_2OH$, *as an acid*, by that for CH_3OH. The pK_a's of methanol and the hydroxymethyl radical in methanol solution are respectively 18.1[21] and about 15.3.[22] Accordingly

(21) (a) Division of K_s, the autoprotolysis constant for methanol ($pK_s = 16.7^{21b}$), by [CH₃OH] gives K_a, and pK_a is 18.1. (b) J. A. Riddick and W. B. Bunger, "Organic Solvents," 3rd ed, Wiley-Interscience, New York, N. Y., 1970, p 145.

Table II. Analysis of the Data of Table I

Series	r^a	Slope[b]	Std. dev., slope	Intercept[b]	Std. dev., intercept	Slope/ intercept	Std. dev., slope/ intercept	k_H^-/k_H^0
A	0.9969	0.525	0.024	0.380	0.017	1.38	0.13	33 ± 3[c]
B	0.9969	0.536	0.024	0.364	0.021	1.47	0.15	35 ± 4[c]
C	0.9988	0.624	0.018	0.321	0.015	1.94	0.15	45 ± 3[d]
D	0.9996	0.584	0.009	0.341	0.006	1.71	0.05	40 ± 1[d]
E	0.9967	0.0971	0.0046	0.0427	0.0039	2.27	0.32	55 ± 8[e]
F	0.9996	0.100	0.0016	0.0427	0.0012	2.34	0.10	56 ± 2[f]

[a] Correlation coefficient. [b] In plot of $[RI](\% \ NH)/(\% \ NI_t)$ vs. $[NaOCH_3]$, where $\% \ NI_t = \% \ NI + \% \ NA$. [c] Based on $[CH_3OH] = 23.7 \ M$. [d] Based on $[CH_3OH] = 23.1 \ M$. [e] Based on $(CH_3OH] = 24.1 \ M$. [f] Based on $[CH_3OH] = 23.8 \ M$.

K_d^-/K_d^0, which expresses the thermodynamic tendency of methoxide ion to dissociate a hydrogen atom, relative to that of methanol, is about 630. The ratio of $\log k_H^-/k_H^0$ to $\log K_d^-/K_d^0$ is about 0.6.

It is instructive to view the methoxide ion as a hydrogen donor of the structural class CH_3Z, and to compare the substituent effect of the ionized hydroxy group, O^-, with that of other Z groups having first atoms with unshared valence shell electron pairs. Although the hydrogen donor reactivities of numerous substances toward the p-nitrophenyl radical have been measured,[5] the hydrogen donors studied do not include many CH_3Z of the type specified. On the other hand, the hydrogen donor reactivities of several such substances toward the phenyl radical are known. The following relative reactivities, for several Z, are of immediate interest: CH_3 (1.0); Cl, 2.3; HO, 4.3; CH_3S, 17; $(CH_3)_2N$, 33. If the reactivity of CH_3O^- were as much greater than CH_3OH toward the phenyl as toward the p-nitrophenyl radical, the figure for Z = O^- would be about 200.

It has been suggested[2] that structures such as **2** make a significant contribution to resonance in the radicals (usually represented as **1**) which result from hydrogen

$$\overset{\cdot}{C}H_2\!\!-\!\!\overset{\cdot\cdot}{Z}\!\!-\!\!R \qquad\qquad \overset{\cdot\cdot}{C}\overline{H}_2\!\!-\!\!\overset{+}{Z}\!\!-\!\!R$$

$$\textbf{1} \qquad\qquad\qquad\qquad \textbf{2}$$

abstraction, and that the resulting stabilization is manifest to some extent in the transition state for hydrogen abstraction. The listed substituent effects are consistent with that generalization, as is the especially large effect of the ionized hydroxy group.

Reactivities of Neopentyl Iodide and Iodobenzene as Iodine Donors. Our data enable the reactivities of these two compounds toward the p-nitrophenyl radical to be compared. Dividing k_{MeOH}/k_{PhI} by k_{MeOH}/k_{neoPI} gives k_{neoPI}/k_{PhI}; making use of ratios given above, k_{neoPI}/k_{PhI} is computed to be 8.3. A similar calculation based on reactivity ratios with methoxide ion gives 5.8. The difference between these estimates stems from differences between the k_H^-/k_H^0 measurements from the iodobenzene runs and the neopentyl iodide runs (Table II).

The relative reactivities of neopentyl iodide and

iodobenzene toward the *phenyl* radical may be estimated from data in the literature. One multiplies k_{neoPI}/k_{Br}[25] (evaluated as 0.24[16]) by k_{Br}/k_{Cl}[25] (evaluated as 257[26]) and divides by k_{PhI}/k_{Cl}[25] (estimated as 16–18[27]) and obtains 3.6 as an estimate of k_{neoPI}/k_{PhI}. Inasmuch as the reactivity ratios used in this computation are for a different aryl radical, at different temperatures (60–80°), and in different solvents, the agreement with estimates from our work is remarkable.

Conceivable Complications. Two types of side reaction require consideration. One is iodine atom capture by or from the products of reaction 3, above. The NI produced by attack of N of iodobenzene or neopentyl iodide may transfer its iodine to another N radical, but that reaction would cause no chemical change. However, if NI yielded iodine to a phenyl or neopentyl radical, reversing reaction 3, the result would be to diminish the apparent yield of NI and to increase that of NH. That complication ought to be greater the greater the concentration of NI in the system, and therefore greater at lower concentrations of methoxide ion (see Table I). The relative decrement in the denominator of $[RI](\% \ NH)/(\% \ NI)$, which is the quantity plotted vertically in Figure 1 (see eq 7), would be proportional to [NI], but the relative increment in [NH] would be greater at lower $[NaOCH_3]$, with consequent increase in the intercept and decrease of the slope of the plot. Unfortunately, we cannot estimate the seriousness of this complication or its relative gravity in the iodobenzene as compared to the neopentyl iodide runs.

Secondly, the hydroxymethyl radical anion, $\cdot CH_2O^-$, produced directly in reaction 2 and indirectly as a result of proton transfer following reaction 1, is a good electron donor[28,29] and may be expected to transfer electrons to several participants in these systems. Probable electron acceptors are NH, NI, iodobenzene, and neopentyl iodide. The radical anions thereby formed from the iodo compounds would expel iodide ion, forming the respective aryl or alkyl radicals, while that from NH would linger, either to act as a radical scavenger or to form ultimately some reduction product.

All four of these electron acceptors are known or can be expected to react with the hydrated electron at

(22) pK_a for $\cdot CH_2OH$ in water is 10.7.[23] For neutral hydroxylic acids, pK_a in CH_3OH is about 4.6 units greater than in water.[24] pK_a of $\cdot CH_2OH$ in CH_3OH is thereby estimated to be 15.3.

(23) K.-D. Asmus, A. Henglein, A. Wigger, and G. Beck, *Ber. Bunsenges. Phys. Chem.*, **70**, 756 (1966); G. P. Laroff and R. W. Fessenden, *J. Phys. Chem.*, **77**, 1283 (1973).

(24) B. W. Clare, D. Cook, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *J. Amer. Chem. Soc.*, **88**, 1911 (1966).

(25) k_{Br} refers to abstraction of bromine from CCl_3Br, and k_{Cl} to abstraction of chlorine from CCl_4.

(26) C. Rüchardt, *Angew. Chem.*, **82**, 845 (1970); *Angew. Chem., Int. Ed. Engl.*, **9**, 830 (1970).

(27) W. C. Danen, D. G. Saunders, and K. A. Rose, *J. Amer. Chem. Soc.*, **95**, 1612 (1973).

(28) K.-D. Asmus, A. Wigger, and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **70**, 862 (1966).

(29) J. F. Bunnett and C. C. Wamser, *J. Amer. Chem. Soc.*, **89**, 6712 (1967).

encounter-controlled rates,[30] but studies of the radical-induced deiodination of aryl iodides in alkaline methanol[29] indicate that NH is a considerably better electron acceptor than iodobenzene. NI should be better yet. It therefore is conceivable that electron transfer and ensuing events may convert some NI to NH, and this complication is likely to be manifest particularly at higher NaOCH₃ concentrations, but we are unable to assess how serious it may be.

A third conceivable complication is arylation of iodobenzene, NH, or NI by nitrophenyl or phenyl radicals. However, arylation is much slower than iodine atom abstraction[12] and is unlikely to make much difference in this system.

Experimental Section

Materials. Anhydrous reagent grade methanol was distilled from magnesium methoxide, and then saturated with dry oxygen-free nitrogen. Oxygen was removed by passing commercial high-purity nitrogen over BASF catalyst R-3-11 (BASF Colors & Chemicals, Inc.). Sodium methoxide solutions were prepared by dissolving clean metallic sodium in methanol under nitrogen, and then filtering through a fine sintered-glass filter under nitrogen; stock solutions were standardized against standard hydrochloric acid solutions (Titrisol).

Iodobenzene was prepared according to the method of Lucas and Kennedy[31] via the diazotization of aniline, followed by treatment with aqueous potassium iodide. Commercial samples have, in the past,[12a] proved too impure for use. The synthetic material was pure by glpc analysis.

Neopentyl iodide was prepared according to the procedure of Beringer and Schultz.[32] Neopentyl tosylate, from the alcohol and

p-toluenesulfonyl chloride in pyridine, was treated with 2 equiv of sodium iodide in refluxing 2-methoxyethanol. Distillation of the product, bp 70° (100 mm), afforded the iodide, which was pure by glpc and nmr analysis.

p-Nitrophenylazo methyl ether was synthesized as described previously by Bunnett and Takayama.[10a]

Product Analysis. The product yield data reported in the tables were determined as follows: 1 ml of a stock solution of iodobenzene or neopentyl iodide was pipetted into a 10-ml volumetric flask. An appropriate volume of ca. 2 M NaOCH₃ solution was added and the flask filled to the mark with methanol. After equilibration at 30.0°, a 0.1-mmol sample of p-nitrophenylazo methyl ether was added and the flask shaken vigorously to dissolve the ether. The solutions were maintained at 30.0° for 16–20 hr, then poured into 50 ml of 0.5 N HCl; 1 ml of a standard solution of p-nitrochlorobenzene in methanol was added and the mixture was extracted with 3 × 20 ml methylene chloride. The extracts were washed with water (25 ml), saturated NaHCO₃ solution (25 ml), and water (25 ml), then dried (Na₂SO₄), and the solvent evaporated. The residue was dissolved in 1.0 ml of methylene chloride and analyzed by glpc. By subjecting known mixtures to this extraction procedure it was shown that there is no selective loss of material.

Glpc analysis of the products was carried out on a Hewlett-Packard Model 5750 gas chromatograph equipped with flame detectors and temperature programming capability. A ¹/₈ in. × 3 ft column of 4% Carbowax 20M on Chromosorb G AW/DMCS was used to separate the products with an air flow of 30 ml/min. A temperature program over the range of 138–168° provided excellent separation and peak shapes. The Hewlett-Packard Model 7123A strip-chart recorder was equipped with an electronic integrator from which areas were determined. Standard solutions of nitrobenzene, p-nitroanisole, p-nitrochlorobenzene, and p-nitroiodobenzene were used to determine relative response factors for each compound. Two or three runs were made for each sample and reproducibility of areas was usually within 2%.

Calculation of Slope and Intercept. The fit of the data to eq 4 was evaluated by linear least-squares analysis on an Olivetti-Underwood Programma 101 calculator.

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Ring-Closure Reactions. II.[1] Kinetics of Six- to Ten-Membered Ring Formation from o-ω-Bromoalkoxyphenoxides

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Abstract: First-order rate constants and activation parameters have been determined for the formation of six- to ten-membered catechol polymethylene ethers from o-ω-bromoalkoxyphenoxides in 75% ethanol solution at reactant concentrations as low as 2 × 10⁻⁴ M or less. No higher order kinetics terms due to polymerization were detected. The expected cyclic ethers formed in essentially quantitative yields under the conditions of the rate measurements, except for the eight- and nine-membered rings. In the latter cases, significant amounts of the isomeric open-chained alkenylphenols were found as by-products, as a result of a competing intramolecular β-elimination reaction. The ring-closure reactivity did not show any minimum in agreement with Ziegler's work. However, the structural effects responsible for a reactivity minimum in other series are shown to give a contribution to the enthalpy of activation. Perhaps the most important result is the observed probability relationship between entropy of activation and chain length of the ring to be formed, which provided the first test for Ruzicka's theory on ring formation.

The strong dependence of intramolecular reactivity on chain length is well recognized. However, quantitative studies on ring-closure reactivity are scanty for seven-membered and higher ring formation. What is available from the earlier literature is a correlation of ring size with yields and, in a few cases, with only approximate rate studies.[2] No significant progress has

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(2) See references cited in ref 1.