occur even in systems where the initial proton transfer is irreversible in a classical sense. This can be explained by a gain in nonfixed energy when the ion approaches the molecule which is sufficient to drive an endothermic proton transfer and to overcome the energy barrier toward nucleophilic displacement. Nucleophilic aromatic substitution at the fluorine bearing carbon atom is only important compared to S_N2 substitution in the 2-fluoroanisole case. This can be taken as an indication that the controlling factor in the reaction is the interaction between the entering nucleophile and the electropositive fluorine-substituted carbon atom.

Attack on the fluorine-bearing carbon atom in the 2-fluoroanisole leads to formation of an F^- ion–molecule complex whose lifetime is long enough to allow reattack on the newly formed molecule. The results obtained further confirm the importance of relatively long-lived ion–molecule complexes formed by primary reactions in gas-phase ion–molecule systems.

Acknowledgment. We thank the Netherlands Organization for Pure Research (SON/ZWO) for financial support.

Registry No. 2-$FC_6H_4OCH_3$, 321-28-8; 3-$FC_6H_4OCH_3$, 456-49-5; 4-$FC_6H_4OCH_3$, 459-60-9; NH_2^-, 17655-31-1; OH^-, 14280-30-9; CH_3O^-, 3315-60-4; $CH_3CH_2O^-$, 16331-64-9; $CH_3CH_3CH_2O^-$, 26232-83-7; $(CH_3)_2CHO^-$, 15520-32-8; $(CH_3)_3CCH_2O^-$, 55091-58-2; F^-, 16984-48-8; CD_3O^-, 51679-31-3.

Reactions of Aryl Diazonium Salts and Alkyl Arylazo Ethers. 9.[†] Studies of the Carbanionic and Free Radical Mechanisms of Dediazoniation of Substituted 2-Chlorobenzenediazonium Salts

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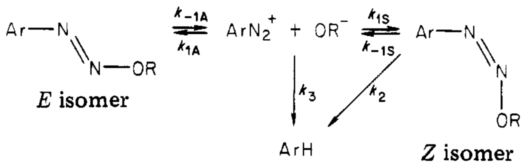
Rate constants for both the decomposition and the *Z–E* interconversion of some substituted 2-chlorophenylazo ethyl ethers in ethanol are reported. In addition, product studies of the decomposition of (2-chlorophenyl)azo methyl ether in the presence of 1,1-diphenylethene and di-*tert*-butyl nitroxide were carried out. On the basis of these results, mechanisms for both anionic and free radical dediazoniation in the basic alcoholic solvents are proposed. A common intermediate, the aryl diimide, formed as a result of hydride ion abstraction from alkoxide ions by the electrophilic terminal nitrogen of the diazonium salt, is proposed for both the anionic and the free radical mechanisms of dediazoniation. The anionic mechanism results from proton abstraction from the aryl diimide by the alkoxide ion. The free radical mechanism results from hydrogen atom abstraction from the aryl diimide by free radicals in solution.

When an aromatic diazonium salt is dissolved in a basic alcoholic solution, the major initial product is the alkyl (*Z*)-arylazo ether.[1,2] This *Z* isomer is, however, unstable, and subsequently it is converted either to the more thermodynamically stable *E* isomer or to the dediazoniation product (ArH, Scheme I).

It has previously been shown that the dediazoniation process can involve either free radical or anionic intermediates.[3] For example reaction in monodeuteriomethanol (CH_3OD) gives rise to deuterated products (ArD) if the reaction involves aryl anion intermediates whereas nondeuterated products (ArH) are formed by the radical mechanism.[3]

The mechanism in a given case depends on the base concentration[3] and on the substituent on the aromatic ring.[3] For all compounds studied to date, reaction of equimolar amounts of diazonium and alkoxide ions result in dediazoniation by the free radical mechanism. In the presence of an excess of alkoxide ions the mechanism depends on the substituent on the aromatic ring. For compounds carrying electron-donating or only weakly electron-withdrawing substituents (e.g., 4-OMe, 4-Me, unsubstituted, or 4-F), the free radical mechanism is observed.[3] For compounds carrying more strongly electron-withdrawing substituents (e.g., 2-Cl, 3-Cl, and 3-NO_2), the ionic mechanism becomes important.[3] In what might be considered the extreme case, compounds carrying either a 2-NO_2 or a 4-NO_2 substituent, reaction by a radical mechanism is observed.[3] It is of interest to determine why the mechanism changes as the substituent is changed. In an attempt to cast some light onto this problem it is necessary to determine for each mechanism whether dediazoniation occurs directly on the *Z* ether or whether prior ionization to the free diazonium ion is required.

Scheme I



From studies of the effect of the solvent on the rate of dediazoniation it had previously been concluded that dediazoniation occurs on the (*Z*)-arylazo ether.[1,4] It was found that reactions involving ionization of alkyl arylazo ethers [k^{-1A}, k^{-1S}, and k_{Z-E}(interconversion)] occur much faster in more polar solvents (e.g., methanol) than in less polar solvents (e.g., ethanol).[1,4] Since the rate of dediazoniation was found to be slightly faster in ethanol than

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[†] Part 8: Broxton, T. J.; Stray, A. C. *Aust. J. Chem.* **1982**, *35*, 961.

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(3) Bunnett, J. F.; Takayama, H. *J. Am. Chem. Soc.* **1968**, *90*, 5173.
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0022-3263/83/1948-0191$01.50/0

in methanol (4-NO_2 compound[1] and 2,5-dichloro compound[5]), it was concluded that dediazoniation, whether by the free radical mechanism (4-NO_2 compound) or the ionic mechanism (2,5-Cl_2 compound), must occur without prior ionization of the (*Z*)-arylazo ether.

More recently is has been reported that the Hammett plot for the dediazoniation of azo ethers derived from substituted 2-nitrobenzenediazonium ions is V shaped.[6] For compounds on the ascending arm of the Hammett plot (e.g., 2-NO_2-4-CF_3, 2-NO_2-4-COC_6H_5, 2-NO_2-4-CN, 2-NO_2-4-SO_2CH_3, and 2,4-$(NO_2)_2$ compounds; $\rho = 5.8$ in ethanol) the rate of dediazoniation was dependent on the base concentration and was faster than the rate of ionization. This is consistent with reaction on the (*Z*)-arylazo ether itself. For compounds on the descending arm of the Hammett plot (e.g., 2-NO_2-4-OCH_3, 2-NO_2-4-CH_3, 2-NO_2, 2-NO_2-4-Cl, 2-NO_2-5-Cl, and 2-NO_2-5-CF_3 compounds; $\rho = -2.0$ in ethanol) the rate of dediazoniation is independent of the base concentration and is slower than the rate of ionization. This is consistent with a process involving prior ionization of the (*Z*)-arylazo ether. Thus, decomposition directly on the (*Z*)-arylazo ether occurs only for compounds bearing very strong electron-withdrawing substituents, for which the rate of ionization is prohibitively slow. For other compounds it would appear that dediazoniation occurs via prior ionization to the free diazonium ion. Such a process seems to be characterized by a negative Hammett ρ value.

The previously observed lack of solvent effect on the rate of dediazoniation could be the result of cancellation of competing solvent effects on the ionization and decomposition (of ArN_2^+) steps.[6]

Several mechanisms have previously been postulated for carbanionic dediazoniation. They include a base-catalyzed elimination (E2) reaction of the (*Z*)-arylazo ether (eq 1 and 2)[3,7] and hydride ion abstraction from methoxide ion by the electrophilic terminal nitrogen of the diazonium salt (eq 3). In either case an aryl diimide or its anion is

$$ArN_2^+ + CH_3O^- \rightleftarrows ArN{=}NOCH_3 \quad (1)$$

$$ArN{=}NOCH_3 + CH_3O^- \rightarrow ArN{=}N^- + CH_2O + CH_3OH \quad (2)$$

$$ArN_2^+ + CH_3O^- \rightarrow ArN{=}NH + CH_2O \quad (3)$$

formed, either of which may decompose in basic solution to yield aryl anion intermediates (eq 4–6).

$$ArN{=}NH + CH_3O^- \rightarrow ArN{=}N^- + CH_3OH \quad (4)$$

$$ArN{=}N^- \rightarrow Ar^- + N_2 \quad (5)$$

$$Ar^- + CH_3OH \rightarrow ArH + CH_3O^- \quad (6)$$

Another mechanistic possibility for carbanionic dediazoniation is that the azo ether may ionize directly to aryl anion and the resonance-stabilized alkoxydiazonium ion (eq 7).[8]

$$ArN{=}NOR \rightarrow Ar^- + RON{=}N^+ \quad (7)$$

We now report the results of kinetic and product studies relevant to the above mechanistic proposals. Previous studies[5] have shown that for alcoholic solvents (e.g., methanol or ethanol) the occurrence of either the radical or the carbanionic mechanism for a given compound is independent of the solvent. Rate constants reported herein were determined in ethanol because this solvent allowed a wider range of compounds (2-Cl-5-Me to 2-Cl-4-NO_2) to be studied than would be possible in methanol. The product studies, however, were carried out in methanol because of the availability of both CH_3OD and CD_3OH.

Table I. Rate Constants for Decomposition (k_D), *Z*–*E* Interconversion (k_{Z-E}), and Ionization (k_{-1S}) of Some Substituted (*Z*)-(2-Chlorophenyl)azo Ethyl Ethers in Ethanol at 10 °C

substituent	σ [a]	10^4k_{Z-E}, s^{-1}	10^4k_D, s^{-1}	10^4k_{-1S}, [b] s^{-1}
4-NO_2	0.78		1.27	0.9 [c]
5-NO_2	0.71		1.22	1.87
4-CN	0.66		2.28	2.35
5-CF_3	0.54 [b]		4.86	9.2
5-CN	0.56	0.08	3.28	4.63
5-Cl	0.37	1.3	12.5	35
4-Cl	0.23	14	33	
5-OCH_3	0.04	84	196	
H	0	95	133	
5-CH_3	−0.07	183	250	

[a] Reference 16b. [b] Reference 10. [c] Extrapolated from Hammett plot.

Table II. Data from Hammett Plots for Reactions of *Z* Ethers Derived from Substituted 2-Chlorobenzenediazonium Salts in Ethanol at 10 °C

reaction	ρ	correl coeff
ionization	-3.8_5	0.991
Z–*E* interconversion	-5.5_4	0.990
decomposition	-2.8_8	0.993

Results and Discussion

Observed rate constants (k_D) for the decomposition of *Z* ethers derived from substituted 2-chlorobenzenediazonium salts in basic ethanol are in Table I. In the cases where a measurable amount of *E* ether was formed, the rate constant for *Z*–*E* interconversion (k_{Z-E}) was also determined. The rate of *Z*–*E* interconversion and the rate of decomposition can both be calculated from the overall rate of loss of *Z*-ether, provided the relative amounts of each reaction (i.e., k_{Z-E}/k_D) can be determined.[1,9] For compounds where no detectable *E* ether was formed ($k_{Z-E} \ll k_D$), the observed rate of loss of *Z* ether was equated to the rate of decomposition.

For comparative purposes the rate constants for the ionization of *Z* ethers (k_{-1S})[10] are also included in Table I. These ionization rate constants were determined by the thiophenolate method,[10] which gives the most accurate result. Other methods, using α-naphtholate ions, give less accurate results due to ionic strength effects.[10]

With the exception of the 2-Cl-4-NO_2 compound, the rate of ionization was found to be faster than the rate of decomposition. Product studies in deuteriomethanol[5] have shown that the 2-chloro-4-nitro compound decomposes by a radical mechanism in the presence of excess methoxide ion (0.5 M CH_3O^-, 0.1 M ArN_2^+). Other substituted 2-chloro compounds,[5] however, decompose by the ionic mechanism (e.g., 2,5-Cl_2, 2-Cl-5-CF_3, 2,4-Cl_2, 2-Cl). Thus, for the compounds which decompose by the ionic mechanism $k_{-1S} > k_D$.

Hammett plots (not shown) gave a good correlation by using σ for all substituents except the 5-CF_3 group. It has previously been shown that the normal σ value for a *m*-CF_3 group (0.43) is not appropriate for reactions of diazonium salts. A value of 0.54 has been calculated for *m*-CF_3 for

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(5) Broxton, T. J.; Bunnett, J. F., unpublished results.

(6) Broxton, T. J.; McLeish, M. J. *J. Org. Chem.* **1982**, *47*, 3673.

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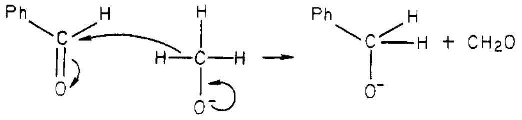
use in diazonium salt reactions.[10,11] Data derived from the Hammett plots are given in Table II. Large negative Hammett ρ values were obtained for the ionization and the *Z*–*E* interconversion reactions. This behavior is consistent with a reaction in which positive charge is being produced in the rate-determining step. For the decomposition reaction the Hammett ρ value is still negative (−2.9), and, although the magnitude is less than for ionization (−3.9) or *Z*–*E* interconversion (−5.5), it does suggest an increase in positive charge in the rate-determining step. This is inconsistent with a mechanism in which it is proposed that the *Z* ether ionizes to aryl anion and alkoxydiazonium cation (eq 7). It is also inconsistent with an E2 reaction on the *Z* ether itself as depicted by eq 2. Both of these mechanisms would require a positive Hammett ρ value, since negative charge is formed on the aryl residue in the rate-determining step of each mechanism.

This leaves us with the mechanism in which free diazonium ion abstracts a hydride ion from methoxide ion (eq 3). An analagous reaction has been proposed in the Cannizzaro reaction.[12] In this case, benzaldehyde abstracts the hydride ion from methoxide ion (eq 8). It therefore seems reasonable that the electrophilic ArN_2^+ could likewise abstract a hydride ion from methoxide ion.



(8)

Starting from the *Z* ether, this mechanism involves an initial ionization to free diazonium ion (k_{-1S}) followed by a partitioning of that diazonium ion between re-formation of the *Z* ether (k_{1S}) and hydride ion abstraction (k_3). Thus, the observed rate of decomposition (k_D) would be defined by eq 9. The formation of free diazonium ion from the

$$k_D = k_{-1S}\frac{k_3}{k_3 + k_{1S}} \qquad (9)$$

Z ether requires a negative ρ value, but this may be modified as a result of the partitioning factor. If the ρ values for reformation of the *Z* ether (k_{1S}) and for hydride abstraction (k_3) are different, then the overall ρ value (k_D) would be different from that observed for the ionization step (k_{-1S}). Thus, a negative ρ value of smaller magnitude than for ionization may be quite reasonable for this mechanism.

As written (eq 1 and 3), this mechanism potentially requires an isotope effect if the reaction is carried out in trideuteriomethanol (CD_3OH). Hydride abstraction from trideuteriomethoxide ion by benzaldehyde has an isotope effect of 2.2.[12] The most economical way to detect this isotope effect would be to use a diazonium salt for which two pathways of decomposition are available. If only one of these pathways required an isotope effect, then the balance between the two pathways should be different in CH_3OD and in CD_3OH. In the presence of 0.5 M $NaOMe/CH_3OD$, 2-chlorobenzenediazonium salt gives chlorobenzene containing ~64% deuterium (Table III). Thus, 64% ionic reaction and 36% radical reaction occurs for this compound under these conditions. Since the ionization rate (k_{-1S}) is greater than the decomposition rate (k_D) and the Hammett ρ value is negative, it seems likely that both the ionic and free radical mechanisms of dediazoniation of the 2-chloro compound occur on the diazonium ion.[6] The most likely mechanism[6] for the radical reaction is electron transfer to the diazonium ion, forming the unstable aryldiazenyl radical ($ArN_2\cdot$) which decomposes to aryl radical and nitrogen. Such a process should not have a solvent isotope effect if the reaction is carried out in CD_3OH. Thus, since the proposed ionic reaction should have an isotope effect, the extent of reaction via the ionic reaction should be reduced (by a factor of at least 2.2 by comparison with the benzaldehyde reaction).

Table III. Results of Product Studies for the Dediazoniation of 2-Chlorobenzenediazonium Salt in Basic Methanol at 23 °C[a]

additive (concn, M)	solvent	yield of chlorobenzene via ionic reaction	yield of chlorobenzene via free radical reaction
	CH_3OD	64	36
	CD_3OH	57	43
DPE (0.11)	CH_3OD	68	4
DTBNO (0.14)	CH_3OD	34	50

[a] [NaOMe] = 0.5 M; $[ArN_2^+]$ = 0.1 M.

It has been found (Table III) that the reaction in CD_3OH gave chlorobenzene containing approximately 43% deuterium. This suggests that there is ~57% ionic reaction and 43% radical reaction (N.B. in CD_3OH, $Ar\cdot \rightarrow ArD$). Thus, the ionic reaction does not show a large isotope effect (64% ionic reaction in CH_3OD; 57% ionic reaction in CD_3OH). Two possible interpretations of this result are either that the ionic reaction does not have an isotope effect (i.e., mechanism involving eq 3 is eliminated) or that both the ionic and radical reactions have a similar isotope effect. Since we could think of no reasonable alternative ionic mechanism at the time, we explored the possibility that the radical reaction experiences an isotope effect in CD_3OH.

One possibility for a radical mechanism involving an isotope effect is a chain process as shown in Scheme II, with steps 11–14 comprising the propagating steps of the chain.

Scheme II

$$ArN_2^+ + CH_3O^- \rightarrow ArN_2\cdot + CH_3O\cdot \qquad (10)$$

$$ArN_2\cdot \rightarrow Ar\cdot + N_2 \qquad (11)$$

$$Ar\cdot + CD_3OH \rightarrow ArD + \cdot CD_2OH \qquad (12)$$

$$\cdot CD_2OH + CD_3O^- \rightarrow \cdot CD_2O^- + CD_3OH \qquad (13)$$

$$ArN_2^+ + \cdot CD_2O^- \rightarrow ArN_2\cdot + CD_2O \qquad (14)$$

One of the propagating steps of this chain reaction (eq 12) would experience an isotope effect in CD_3OH and thus the overall reaction should also.

To determine if the radical dediazoniation of the 2-chloro compound was a chain process, we studied the effect of added radical scavengers 1,1-diphenylethene (DPE) and di-*tert*-butyl nitroxide (DTBNO) on the reaction (see Table III). If the balance between ionic and radical reactions for the 2-chloro compound involves partitioning of the diazonium salt between hydride abstraction and electron acceptance, then this balance should be upset by the addition of radical scavengers if the radical reaction is a chain process.

If a radical trap (e.g., DPE)[13] is added to the reaction mixture then the chain carrying aryl radicals will be trapped and the radical reaction inhibited. This should

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[12] Swain, C. G.; Powell, A. L.; Lynch, T. J.; Alpha, S. R.; Dunlap, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 3584.

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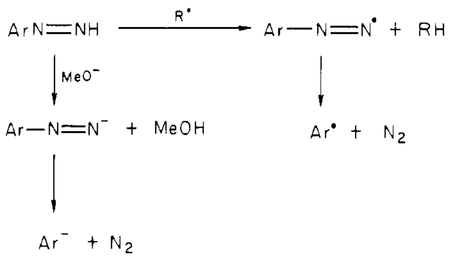
Scheme III



result in increased reaction via the ionic mechanism. Reaction in the presence of 0.5 M MeO$^-$ and 0.11 M DPE in CH$_3$OD resulted in a reduced yield (72%) of chlorobenzene. The chlorobenzene formed, however, had a higher deuterium content (95%) than that from the reaction in the absence of DPE (64% D). Thus, the yield of the free radical reaction product is reduced from 36% to 4% by the addition of 0.11 M DPE to the reaction mixture. The yield of the product of the ionic reaction is not significantly changed. This indicates that the radical mechanism is not a chain process. The aryl radicals are effectively trapped but the amount of reaction via the ionic mechanism is not increased accordingly.

The effect of 0.13 M DTBNO on the reaction was more complicated. Although DTBNO is reported to be an efficient radical trap,[14,15] the yield of product of the radical reaction was in fact increased (36% to 50%). A corresponding decrease in the yield of the product from the ionic reaction (64% to 34%) was observed. The total yield of chlorobenzene in the presence of DTBNO was only 84%. Thus, partial trapping of the aryl radical has occurred. It appears that DTBNO facilitates the radical reaction. This also is inconsistent with the operation of a chain process because DTBNO has frequently been shown to be an efficient inhibitor of chain reactions.[14,15]

An alternative possibility for a radical mechanism requiring an isotope effect is that hydride abstraction from methoxide ion is also the first step for that mechanism. The partitioning between ionic and radical reactions may then occur on the aryl diimide product (ArN=NH).

This mechanistic scheme requires competition between methoxide ion and radical species for the aryl diimide and explains the incursion of the ionic mechanism at higher methoxide concentrations for compounds capable of stabilization of the anion produced. Furthermore, it provides a viable radical process which is not a chain reaction.

The lack of a solvent effect on the rate of dediazoniation by either the anionic or the free radical process can now be explained in terms of the combination of solvent effects on the rate of ionization of the *Z* ether (k_{-1S}) and on the hydride ion abstraction (k_3) by the diazonium ion. According to the Hughes–Ingold solvent theory,[16a] an increase in solvent polarity would increase the rate of ionization (charge formed in rate-determining step) but should decrease the rate of hydride ion abstraction (charge destroyed in rate-determining step). Thus, the solvent effect on the overall dediazoniation rate (k_D, eq 9) cancels out.

The effect of DPE on the partitioning of the aryl diimide intermediate (Scheme III) would be negligible because even if the aryl radicals are trapped, the product radical (PhCH$_2$–CPh$_2\cdot$) should still be able to abstract the hydrogen from the diimide. Thus, the percentage of radical reaction (and hence, ionic reaction) remains constant.

Added DTBNO, itself a free radical, decreases the percentage of ionic reaction, possibly because this radical is able to compete with methoxide ion for the hydrogen on the aryl diimide. Thus, the radical reaction prospers at the expense of the ionic reaction.

Formaldehyde radical anions have been detected in reaction mixtures involving the free radical pathway.[5] It now appears that they are not involved in the actual partitioning of the aryl diimide. They are merely byproducts formed from the interaction of the aryl radicals with the solvent in the presence of base (see eq 11–13 in Scheme II).

Further work is underway to try to obtain definitive evidence in favor of the reaction mechanism shown in Scheme III.

Conclusion

(1) Both radical and ionic dediazoniation reactions occur on the free diazonium ion rather than on the *Z* ether. (2) The first step of both dediazoniation reactions involves hydride ion abstraction by the diazonium ion from the alkoxide ion. (3) Partitioning between the ionic and radical mechanisms occurs at the aryl diimide stage (ArN=NH). (4) The radical process is not a chain reaction. (5) Although formaldehyde radical anions have been detected in the reaction system, they are not involved in the actual dediazoniation process.

Experimental Section

Materials. The required diazonium salts were prepared by diazotization of the corresponding anilines as described by Bunnett.[17] 2-Chloro-, 2-chloro-5-methoxy- (6-chloro-*m*-anisidine as HCl salt), 2,4-dichloro-, 2,5-dichloro-, 2-chloro-5-(trifluoromethyl)-, 2-chloro-5-nitro-, and 2-chloro-4-nitroaniline (Aldrich), 2-chloro-5-cyanoaniline (3-amino-4-chlorobenzonitrile; Transworld Chemicals), and 2-chloro-5-methylaniline (3-amino-4-chlorotoluene; ICN Pharmaceuticals) were commercially available. 2-Chloro-4-cyanoaniline was available from a previous study.[10]

Alkyl (*Z*)-arylazo ethers were prepared in situ by mixing precooled solutions of diazonium and alkoxide ions at 10 °C.

Ethanol and methanol were dried by treatment with the corresponding magnesium alkoxide.[18]

1,1-Diphenylethene and monodeuteriomethanol (CH$_3$OD; Aldrich), di-*tert*-butyl nitroxide (Kodak), and trideuteriomethanol (CD$_3$OH; Merck) were commercially available.

Kinetic Measurements. The rates of dediazoniation (k_D) and *Z–E* interconversion (k_{Z-E}) were determined by a sampling technique using *N*-(1-naphthalene)ethylenediamine (NED), as described previously.[1,19]

Product Studies. The diazonium salt (0.2 g) was dissolved in the basic alcoholic solvent (e.g., CH$_3$O$^-$/CH$_3$OD or CD$_3$O$^-$/CD$_3$OH; 10 mL, 0.5 M methoxide). The mixture was stirred for 16 h at room temperature. Then a solution of a suitable standard (e.g., *p*-dichlorobenzene for the 2-chlorobenzenediazonium salt; 1 mL, 0.27 M) was pipetted into the reaction mixture. The mixture was thoroughly mixed, and a sample was analyzed either by gas–liquid chromatography (Hewlett-Packard Model 5710A; for yield determination) or by gas chromatography–mass spectroscopy (for determination of the deuterium content of the product; JEOL DMS-100 mass spectrometer). In both cases, a 6-ft glass column containing 3% OV-1 on Gas Chrom Q was used. Similar results were obtained from samples that had been poured onto ice, acidified, and extracted (Et$_2$O). The organic extract was washed (H$_2$O), dried (MgSO$_4$), and concentrated to approximately

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(16) Hine, J. "Physical Organic Chemistry"; McGraw-Hill: New York, 1962: (a) p 73; (b) p 87.

(17) Bunnett, J. F.; Takayama, H. *J. Org. Chem.* **1968**, *33*, 1924.

(18) Vogel, A. I. "A Textbook of Practical Organic Chemistry", 3rd ed.; Longmans Green and Co.: New York, 1961; p 169.

(19) The rate of *Z–E* interconversion was previously called the rate of protection (k_P).[1]

1 mL before analysis. The extent of monodeuteration of the product was calculated after allowance had been made for the natural abundance of carbon-13, nitrogen-15, and deuterium.

Product studies in the presence of DPE and DTBNO were carried out as described above. The diazonium salt (0.2 g) was dissolved in basic alcoholic solvent (10 mL, 0.5 M CH_3O^-/CH_3OD) containing either DPE (0.2 g) or DTBNO (0.2 g). In the reactions using DTBNO, nitrobenzene was used as an internal standard in place of *p*-dichlorobenzene because *p*-dichlorobenzene and DTBNO had the same retention time on the column being used.

Acknowledgment. We are pleased to acknowledge the assistance of Mr. J. Smith of the Department of Physical Chemistry, La Trobe University, with the gas chromatography–mass spectral analyses.

Registry No. CH_3OH, 67-56-1; EtO^-, 16331-64-9; CH_3O^-, 3315-60-4; DPE, 530-48-3; DTBNO, 2406-25-9; (*Z*)-(2-chloro-4-nitrophenyl)azo ethyl ether, 82765-37-5; (*Z*)-(2-chloro-5-nitrophenyl)azo ethyl ether, 82765-40-0; (*Z*)-(2-chloro-4-cyanophenyl)azo ethyl ether, 82765-43-3; (*Z*)-[2-chloro-5-(trifluoromethyl)phenyl]azo ethyl ether, 82765-39-7; (*Z*)-(2-chloro-5-cyanophenyl)azo ethyl ether, 82765-41-1; (*Z*)-(2,5-dichlorophenyl)azo ethyl ether, 82765-38-6; (*Z*)-(2,4-dichlorophenyl)azo ethyl ether, 83844-94-4; (*Z*)-(2-chloro-5-methoxyphenyl)azo ethyl ether, 83844-95-5; (*Z*)-(2-chloro-5-methylphenyl)azo ethyl ether, 83844-96-6; (*Z*)-(2-chlorophenyl)azo ethyl ether, 83844-97-7; ethanol, 64-17-5; 2-chlorobenzenediazonium, 17333-83-4.

Poly(ethylene glycols) and Poly(ethylene glycol)-Grafted Copolymers Are Extraordinary Catalysts for Dehydrohalogenation under Two-Phase and Three-Phase Conditions[1]

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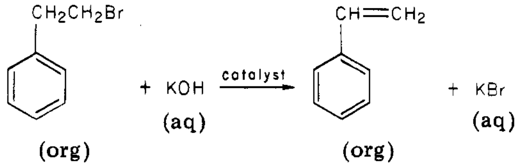
Poly(ethylene glycols) [$HO(CH_2CH_2O)_nH$, where $n > 3$] possess remarkably high activity as catalysts for dehydrohalogenation in organic–aqueous hydroxide two-phase systems, relative to classical phase-transfer agents, i.e., benzyltriethylammonium chloride and 18-crown-6. The importance of terminal hydroxyl groups together with the abrupt increase in catalyst activity and concentration in the organic layer on going from $n = 2$ to $n = 3$ and from $n = 3$ to $n = 4$ suggests the involvement of novel polymeric alkoxides I and/or hydroxides II. Moreover, the fact that maximum activity is obtained with $n \geq 5$ implies that an "18-crown-6-like" structure occurring at the terminus of the polymer chain is optimal for catalysis. Poly(ethylene glycols) grafted to cross-linked polystyrene display reasonably high activity. In preparative-scale conversions, such triphase catalysts can be recovered quantitatively by simple filtration and reused without significant loss in activity.

Phase-transfer catalysis is now established as a versatile and important synthetic technique in organic chemistry.[2] Surprisingly, however, few practical applications have been devised for dehydrohalogenation reactions and elimination processes in general. Under liquid–liquid conditions, conventional phase-transfer agents (e.g., tetraalkylammonium salts) yield synthetically useful procedures only when employed in stoichiometric quantities.[3,4] We have recently discovered that simple poly(ethylene glycols) [$HO(CH_2CH_2O)_nH$, where $n > 3$] possess extraordinary activity for *catalyzing* dehydrohalogenation in organic–aqueous hydroxide two-phase systems.[5,6] We now present the details of these findings and propose the involvement of novel polymeric alkoxides and/or hydroxides as the active catalyst(s). We further show that poly(ethylene glycols) grafted to cross-linked polystyrene yield attractive alternate procedures based on the triphase catalysis principle.[7]

Results

Liquid–Liquid Two-Phase Dehydrohalogenation. In order to compare catalyst efficiency for dehydrohalogenation, we chose the conversion of (2-bromoethyl)benzene to styrene as the standard reaction (eq 1). This organic halide has a reasonable tendency to undergo elimination and produces a single olefinic product.



(1)

In the absence of a catalyst, benzene solutions of (2-bromoethyl)benzene afforded no detectable styrene after vigorous stirring with 60% aqueous potassium hydroxide for 24 h at 35 °C. In the presence of 10 mol % of benzyltriethylammonium chloride, a 17% yield was obtained after 21 h. When pentaethylene glycol was employed (10 mol %), analysis of the organic layer (GLC) revealed a 63% conversion after 8 min! Table I lists observed pseudo-first-order rate constants plus catalyst and base content

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