Disproportionation of the Technetate Ion in Aqueous

Alkaline Media. An Electrochemical Study¹

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The objective of this paper is to elucidate the primary reduction process when pertechnetate ion is electrochemically reduced in alkaline media. Using the techniques of coulometry (at controlled potential), chronoamperometry, and double potential step chronoamperometry we have demonstrated that technetate ion is produced at the electrode surface when gelatin is present in solution and then undergoes rapid disproportionation

$$\operatorname{TcO}_{4}^{-} \xrightarrow{e^{-}} \operatorname{TcO}_{4}^{2-}$$
$$\operatorname{TcO}_{4}^{2-} \longrightarrow \operatorname{TcO}_{4}^{-} + \operatorname{TcO}_{4}^{3-}$$

where $k \approx 1.5 \times 10^5$ l. mol⁻¹ sec⁻¹ (when ionic strength is 1). If this mechanism obtains, then the following thermodynamically favored reaction must be kinetically blocked

$$TcO_4^2 - \stackrel{e^-}{\longleftarrow} TcO_4^3 -$$

In the technetium system gelatin seems to be the blocking agent; in the absence of gelatin, production of the technetate ion is bypassed and we observe

$$TcO_4 \xrightarrow{2e^-} TcO_4^{3-}$$

The dependence of the disproportionation rate constant on ionic strength confirms that the reacting species is doubly charged. The small dependence on temperature and pH (in the alkaline region) suggests that the kinetics are proceeding near the diffusion-controlled limit. The rate constant k (1.5 × 10⁵ l. mol⁻¹ sec⁻¹), though considerably lower than the commonly accepted limiting value of 10¹⁰ l. mol⁻¹ sec⁻¹, is not unreasonable when the charges of the reacting ions are considered.

A large body of literature has evolved describing the investigations of the chemistry of technetium and has been reviewed in several fairly recent publications.²⁻⁵ Several workers have studied the electrochemical behavior of TcO_4^- in aqueous alkaline media and have presented various data^{8,6-11} (predominantly polarographic and coulometric). Two marked polarographic waves are observed. The first one corresponds to a two-⁸⁻¹¹ or three-electron^{6,7} change. Coulometry at potentials at the "knee" of the first wave or just barely on the plateau unambiguously indicates a three-electron change^{8,6} in aqueous alkaline media. There is some evidence that the second wave represents an additional one-electron change.^{6,7,10,11}

The objective of this paper is to elucidate the primary reduction process (*i.e.*, details of the first wave) when pertechnetate ion is electrochemically reduced in alkaline media. No previous studies have produced real kinetic information. The search for the technetate ion (TcO_4^{2-}) as the first reactive intermediate in the reduction sequence was prompted by two facts: the existence of several Tc (VI) compounds¹² and the wellcharacterized and stable (in strongly alkaline media) manganate ion. Using the techniques of coulometry (at controlled potential), chronoamperometry,¹³ and double potential step chronoamperometry,¹⁴ we have demonstrated that

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⁽³⁾ R. A. Pacer, "Investigation of the Analytical Chemistry of Technetium," University Microfilms, Inc., Ann Arbor, Mich., 1966.

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technetate ion is produced at the electrode surface when gelatin is present in solution and then undergoes rapid disproportionation

$$TcO_4^- \stackrel{e^-}{\swarrow} TcO_4^{2-}$$
 (1)

$$2\mathrm{TcO}_{4^{2}} \xrightarrow{\kappa} \mathrm{TcO}_{4^{-}} + \mathrm{TcO}_{4^{3}} \xrightarrow{(2)}$$

where $k \approx 1.5 \times 10^5$ l. mol⁻¹ sec⁻¹. It has been pointed out elsewhere^{15,16} that if this mechanism obtains, then the following thermodynamically favored reaction must be kinetically blocked

$$TcO_4^2 - \stackrel{e^-}{\longleftarrow} TcO_4^3 -$$
 (3)

In the technetium system gelatin seems to be the blocking agent; in the absence of gelatin, production of the technetate ion is bypassed and we observe

$$TcO_4^- \xrightarrow{2e^-} TcO_4^{3-}$$
 (4)

The dependence of the disproportionation rate constant on ionic strength confirms that the reacting species is doubly charged. The small temperature pH dependence (in the alkaline region studies) suggests that the kinetics are proceeding near the diffusion-controlled limit. The rate constant k (1.5 × 10⁵ l. mol⁻¹ sec⁻¹), though considerably lower than the commonly accepted limiting value of 10¹⁰ l. mol⁻¹ sec⁻¹, is not unreasonable when the charges of the reacting ions are considered.

Theory

The calculations establishing the chronoamperometric current-kinetic-time relationship for the disproportionation mechanism have been presented previously.^{16,17} We present here the additional theoretical relationship for double potential step chronoamperometry¹⁴ as calculated by digital simulation.¹⁸ The basic assumptions for these calculations are that the diffusion coefficients of all species are the same and that the rate of disappearance of species B (reaction 2) is expressed

$$\frac{\mathrm{d}(\mathrm{B})}{\mathrm{d}t} = -2k(\mathrm{B})^2 \tag{5}$$

The "2" in the second term of this expression appears because 2 molecules of species B are removed per reaction. This has been a point of general inconsistency in discussions of disproportionation reactions. The working curves (Figure 1) are plots of

$$\frac{i_{t_r}}{i_{\tau/\epsilon t_f}} vs. \log (kt_f C)$$
(6)

 $\frac{t_r}{t_f} = \frac{1}{4}, \frac{1}{2}, \frac{3}{4}, 1 \tag{7}$

where t_i is the time measured from initiation of the first potential step, and t_r is the duration of the second poten-



Figure 1. Working curves for double potential step chronoamperometry of a disproportionation mechanism. The four curves (from top to bottom) are for $t_r/t_f = 1/4$, 1/2, 3/4, and 1.

tial step $(t_r = 0$ when $t = t_i)$. The forward current is recorded at $\frac{7}{8t_f}$ because of the nature of the digital data acquisition system. Each of the four working curves is at a set ratio t_r/t_f . The dimensionless parameter kt_fC is the product of the second-order rate constant, t_f , and the bulk concentration of the initial species.

Experimental Section

Reagents and Apparatus. The technetium (Tc⁹⁹) used in these experiments was obtained as the ammonium pertechnetate solution from Oak Ridge National Laboratory. The concentration of the stock solution was determined using the spectrophotometric method of Wolkowitz.¹⁹ The NaOH was reagent grade, and the water was doubly distilled.

The electrochemical cell was water-jacketed and maintained at $T \pm 0.1^{\circ}$, (where $T = 20, 25, 30, \text{ or } 35^{\circ}$). The test electrode was a specially constructed dme adjusted to yield a mercury-flow rate of ~ 0.18 mg/sec (this *m* value was periodically checked) and a drop time of about 1 min. The capillary was 36 in. of marine barometer tubing²⁰ bent into a figure 4. To avoid the large *iR* drop of such a long column, a 10-mil

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for

platinum wire was sealed into the capillary about 1 cm from the lower end. This was accomplished by applying 25–30 lb of air pressure at the far end of the capillary and heating the desired spot on the capillary wall until it blew out. By placing a small bead of soft glass about 1/8 in. from the end of the Pt wire, the wire was easily sealed into the capillary. When filling the capillary with mercury, care was taken to fill the cavity completely at the seal point. When the capillary was operating properly, the mercury column did not pull back after the drop fell off. The platinum lead was shielded from the solution by covering the seal and the lower part of the capillary with a shrinkable polyolefin tubing.²¹ The polyolefin tended to react slowly with alkali and was in turn covered with shrink Teflon tubing.²² The Teflon did not form as tight a seal as the polyolefin tubing and was not used alone.

The calomel reference electrode was separated from the test solution by a salt bridge containing only supporting electrolyte (of the same concentration as in the test solution). No Luggin capillary was used. The auxiliary electrode was a platinum wire ring ~ 1 in. in diameter located with the dme centered as well as possible. Prepurified argon, passed over hot copper, was used for degassing solutions. The potentiostat (with current amplifier and positive feedback for *iR* compensation) was constructed according to the general design of Lauer and Osteryoung.²³ The response time of this cell-potentiostat combination was such that reliable data were obtained only after approximately 500 µsec.

The data acquisition system is fundamentally the same as that described by Booman.²⁴ Sampling times are selected according to a binary sequence rather than the logarithmic sequence of Booman. An RC clock puts out a pulse train of adjustable frequency; a given pulse initiates both the sampling sequence and the potential step. If Δt is the time between pulses, then the sampling occurs at the time intervals cited in Chart I. The numbers with asterisks represent those times at which a second potential step can be initiated.

Calute in State in St	Chart I :	Data	Acquisition	Sampling	Times,	Δt
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$\Delta t(1,$	2,	3,	4,
5,	6,	7,	8,*
10,	12,	14,	16,*
20,	24,	28,	32,*
40,	48,	56,	64,*
80,	96,	112,	128,*
160,	192,	224,	256, *
320,	384,	448,	512, *
640,	768,	896,	1,024,*
1,280,	1,536,	1,792,	2,048,*
2,560,	3,072,	3,584,	4,096,*
5,120,	6, 144,	7,168,	8,192,*
10,240,	12,288,	14,336,	16,384,
20,480,	24,576,	28,672,	32,768,
40,960,	49,152,	57,344,	65,536,
81,920.	98,304,	114,688)	

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The current reading at that particular time is always extremely high, because of the high charging current induced by the potential step. Thus when using the double potential step technique the last meaningful current reading during the first potential step will be at a time $\frac{7}{8t_1}$. In all the work presented here the RC clock frequency was adjusted so that $\Delta t = 100 \,\mu\text{sec}$, giving a dynamic time range from 10^{-4} to 11.5 sec. The actual acquisition time aperture is less than 1 μsec . The analog to digital conversion, however, requires about 70 μsec .

The readouts are stored in a buffer, and after the experiment is completed they are printed out on a teletype printer and/or punch tape. Appropriate coded instructions can be typed in. After the punch tape has been converted to magnetic tape (CDC 924) the desired operations can be carried out by the CDC 6600: *e.g.*, calculation of apparent n after spherical and drop growth corrections²⁵ and data plotting.

Procedure. Three types of experiments were carried out: coulometry at controlled potential, chronoamperometry, and double potential step chronoamperometry. The results of the coulometry at a mercury pool and in 1 M NaOH indicate that as long as the electrolysis potential is not more negative than about -1.0 V vs. see the reduction process requires three electrons per molecule of TcO₄⁻ (3.1 electrons at -1.00 V). This is in accord with observations of other workers who noted a three-electron process throughout the alkaline region^{3,6}

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(25) The correction for spherical diffusion was made using the modified Cottrell equation presented by Delahay (P. Delahay, "New Instrumental Methods of Analysis," Interscience Publishers, New York, N. Y., 1954)

apparent
$$n = \frac{\pi^{1/2} i t^{1/2}}{F A D^{1/2} C} \left[\frac{1}{1 + \frac{\pi^{1/2} D^{1/2} t^{1/2}}{r_0}} \right]$$
 (F1)

where r_0 is the radius of the electrode and all other terms have their usual significance.

The correction for drop growth was calculated using digital simulation

apparent
$$n \simeq \frac{\pi^{1/2it^{1/2}}}{FA_{\text{start}}D^{1/2}C} \left[\frac{1}{1+\frac{t}{t_{\text{start}}}}\right]$$
 (F2)

where t is the duration of the chronoamperometric experiment, t_{start} is the time in drop life at which the potential step was initiated, and A_{start} is the electrode areas at t_{start} . This equation is valid within 2% if

$$\frac{t}{t_{\text{start}}} \le 0.2 \tag{F3}$$

We simultaneously correct for the two effects (growth and spherical) by combining eq F1 ad F2 to give

apparent
$$n \cong \frac{\pi^{1/2} i t^{1/2}}{FAD^{1/2}C} \left[\frac{1}{1 + \frac{\pi^{1/2} D^{1/2} t^{1/2}}{r_0}} \right] \left[\frac{1}{1 + \frac{t}{t_{\text{start}}}} \right]$$
(F4)

A similar linear combination was first suggested by J. R. Delmastro and D. E. Smith, Anal. Chem., 38, 169 (1966).



Figure 2. Dependence of apparent n on the step potential for $1.068 \times 10^{-3} M \text{ TcO}_4$ in 1 M NaOH and 0% gelatin.



Figure 3. Dependence of apparent n on the step potential for 1.068 M TcO₄⁻ in 1 M NaOH and 0.005% gelatin.



Figure 4. Dependence of apparent n on the step potential of 1.068 M TcO₄⁻ in 1 M NaOH and 0.02% gelatin.

and a four-electron process at slightly more negative potentials $(E \simeq -1.1 \text{ V})$;⁶ at -1.27 V the number of electrons becomes large (e.g., ~ 30) and the process appears to be catalytic. It is clear that several complicating phenomena are introduced at the more negative potentials; we confine ourselves to a study of the primary reduction process occurring in the vicinity of -1.0 V.



Figure 5. Dependence of apparent n on the step potential of 1.068 M TcO₄⁻ in 1 M NaOH and 0.04% gelatin.



Figure 6. Apparent n dependence on gelatin for step potential of -1.00 V vs. sce.

Chronoamperograms were run on a variety of solutions: the variable quantities were the magnitude of the potential step; the concentrations of the NaOH, NaClO₄, NH₄⁺, TcO₄⁻, and gelatin; the ionic strength (usually maintained at 1.0, except where noted); and the temperature.

The data are presented in several forms. Figures 2-5 are plots of apparent *n* as a function of the electrode potential. (The calculation of apparent n^{24} requires that one know the diffusion coefficient of TcO_4^- in these media.) We used Astheimer's value of $1.27 \times$ 10^{-5} cm²/sec. The time at which the current was measured is the same for all points on a given curve. For obvious reasons we shall refer to this as a polarogram. The most striking fact in these polarograms is that, at short times in the absence of gelatin, apparent n = 2 and shifts to a value of about 1.0 when the gelatin concentration is >0.005%. By selecting an electrode potential (for the potential step) which corresponds to a plateau value with or without gelatin (e.g., -1.0 V seems the best compromise—see Figures 2-5), we measured apparent n at a particular time (1.6)

		Co	ncentration, M ^a			$k. \text{ mol}^{-1}.$
Run no.	Figure	NH4+TcO4-	NaOH	NaClO ₄	T, C°	sec ^{-1b}
1	9	1.068×10^{-3}	0.10	0.90	25.0	$1.2 imes10^{5}$
2		$1.068 imes10^{-3}$	0.001	1.0	25.0	$1.9 imes 10^5$
3		$3.204 imes10^{-3}$	0.01	0.99	25.0	$1.2 imes10^5$
4		1.608×10^{-8}	0.01	0.99	20.0	$1.5 imes10^{5}$
5	8	$1.068 imes 10^{-3}$	0.01	0.99	25.0	$1.5 imes10^5$
6		$1.068 imes 10^{-3}$	0.01	0.99	30.0	$1.6 imes10^{5}$
7		1.068×10^{-3}	0.01	0.99	35.0	$1.7 imes10^5$
8		$1.068 imes 10^{-3}$	0.01	0.09	25.0	$3.6 imes10^4$

Table I: Summary of Kinetic Data

^a Analytical concentrations: assume $NH_4^+ + OH^- \rightarrow H_2O + NH_3$, and NH_3 is completely removed from the solution. ^b Because of instrumental limitations at short times and chemical complications at longer times there is good experimental-theoretical correlation only within a limited time range (see Figures 8 and 9). Thus we feel that an error analysis of the curve fitting based on some arbitrary criteria would not be particularly meaningful. Repetition of an entire experiment, however, gives a reproducible value of the rate constant within $\pm 10\%$.

msec) as a function of gelatin concentration (Figure 6). The shift of apparent n from 2 to 1 is clear. Similar results were obtained with two concentrations of pertechnetate (3.204 and 1.068 mM). The similarity of the two curves for the two concentrations indicates that the gelatin effect is a surface phenomenon and not the result of a gelatin-pertechnetate complex. Reducing the concentration of NaOH did not produce any marked change; it did, however, appear to require slightly more gelatin to bring apparent n down to a value of 1. Later work indicated that it was advisable to use the minimum quantity of gelatin (about 0.005%) which would give the desired effect. Too much gelatin made it impossible to obtain the reverse chronoamperogram (corresponding to the reversal of reaction 1) prior to mercury dissolution.

Chronoamperograms obtained at the plateau potentials for a variety of solutions are shown in Figure 7. Only qualitative comments are justified. In the presence of gelatin and at lower NaOH concentrations (Figure 7, curves 4-6) there is clear indication of a possible disproportionation reaction as the value of apparent nshifts from 1 to 2. At higher NaOH concentrations the disproportionation reaction appears to be slower. At higher NaOH concentrations (all curves but 4 and 5) the apparent n for the second reaction seems to limit close to three (curves 1, 3, 7). This coincides with coulometric data. The decrease in apparent n at longer times is probably due to electrode filming. We will concentrate, however, on the elucidation of the disproportionation reaction.

Quantitative kinetic data were obtained using the double potential step technique and are shown in Figures 8 and 9; the results are tabulated in Table I. Even with a low gelatin concentration (0.005%) it was impossible to obtain data for 1 *M* NaOH solutions.

Discussion

As the various data plots indicate, the chemistry of



Figure 7. Chronoamperograms of $1.068 \times 10^{-8} M \text{ TcO}_4^{-1}$:

	Step		NaClO4,	
Curve	potential, V	NaOH, M	M	% gelatin
1	-0.92	0.01	0.99	0
2	-0.96	0.10	0.90	0
3	-0.96	1.00	0.0	0
4	-1.08	0.0020	1.0	0.02
5	-1.08	0.01	0.99	0.02
6	-1.04	0.10	0.90	0.005
7	-1.08	1.0	0	0.005

technetium is extremely complex. The poor correlation of theoretical and experimental data at longer times (Figures 8 and 9) is probably indicative of the formation of additional redox products. A quasi-reversible disproportionation would give similar behavior (*i.e.*, increasing values of $i_{t_c}/i_{7/4t_1}$) but would not exhibit the large variation with potential that we observe. Thus we feel that we have isolated the primary reduction process: without gelatin

$$2e^{-} + TcO_4^{-} \longrightarrow TcO_4^{3-} \tag{8}$$

or with gelatin

$$e^- + TcO_4^- \rightleftharpoons TcO_4^{2-}$$
 (quasi-reversible) (9)

DISPROPORTIONATION OF THE TECHNETATE ION

$$2\mathrm{TcO}_4{}^2 - \xrightarrow{k} \mathrm{TcO}_4 - + \mathrm{TcO}_4{}^3 - \tag{10}$$

There appear to be subsequent electron transfers undoubtedly following some chemical transformation of TcO_4^{3-} (see ref 11 for some possible reaction sequences).



Figure 8. Double-step chronoamperograms of pertechnetate ion under varying conditions. Gelatin concentration is 0.005%in 0.01 *M* NaOH and 0.99 *M* NaClO₄.

The data for two runs at different ionic strengths (Table I, runs 5 and 8) show an increase in rate with higher ionic strengths. In the absence of specific ion effects this may be assumed to indicate that the charge on each of the reacting species is of the same sign.²⁶ The high ionic strengths (beyond the range of the Debye-Hückel theory) required by this type of electrochemical experiment precludes using a plot of log k vs. \sqrt{u} ²⁶ (u is ionic strength) to determine the magnitude of the charge on the species. However, the charge can be estimated. The activity coefficient of an ionic species, i, in the presence of excess supporting electrolyte may be expressed by an equation of the form

$$-\log \gamma_i = z_i^2 g_u \tag{11}$$

The constant g_u depends on ionic strength and can be estimated from tables of mean activity coefficients²⁷ where

$$g_u = -\log \gamma_u^{\pm} \tag{12}$$

for a univalent-univalent supporting electrolyte. From the equation

$$k = k_0 \frac{(\gamma_{\rm TcO_4}^2)^2}{\gamma_{\rm (TcO_4)_2}^{4-}}$$
(13)



Figure 9. Double-step chronoamperograms of pertechnetate ion under varying conditions. Gelatin concentration is 0.005% in 0.1 *M* NaOH and 0.9 *M* NaClO₄.

where k_0 is the rate at infinite dilution, and $\gamma_{T_0O_4}^{2-}$ and $\gamma_{(T_0O_4)2}^{4-}$ are the activity coefficients of the technetate ion and of the activated complex, one can derive

$$\log \frac{k}{k_0} = 2g_u z_{\mathrm{TeO_4}^2} - 2$$
(14)

Given two rate constants k_{u_1} and k_{u_2} measured at two ionic strengths u_1 and u_2 , we can write

$$z_{\text{ToO}_4^{2-}} = \left[(\log (k_2 - u_1 / k_{u_2})) (2(g_{u_1} - g_{u_2})) \right]^{1/2}$$
(15)

Using the kinetic data from runs 5 and 8 (Table I) and the values of g_u calculated for 1.0 and 0.1 *M* NaClO₄ (0.202 and 0.111, respectively), we obtain

$$z_{\rm T_{\rm cO_4}^{2-}} = 1.85 \tag{16}$$

The expected value, of course, is 2, and the value of k_0 (from eq 14) is about 4×10^3 .

The small temperature and pH dependence of the disproportionation rate constant suggests diffusion control. The low value of k_0 (relative to the commonly accepted diffusion-controlled frequency factor $k_d = 10^{10}$ l. mol⁻¹ sec⁻¹) may indicate that some activation control exists, obscured by experimental uncertainties and compensating physical phenomena. However, frequency factors considerably smaller than k_d can be qualitatively explained by the increase in free energy

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⁽²⁷⁾ R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, Academic Press, New York, N. Y., 1959.

when two infinitely separated like-charged species are brought together to reaction distance.²⁶

Although we feel confident that our proposed mechanism for the disproportionation of the technetate ion is basically correct, the nature of the subsequent reactions remains ambiguous. Gelatin, which plays an important role in the primary reduction process, no doubt effects other changes in the redox behavior of technetium. The formation of the TcO_2 precipitate also complicates interpretation of the electrochemical data.

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The Reaction of Nitrosonium Nitrate with Isobutylene at 77-195°K¹

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The reactivity of nitrosonium nitrate toward some unsaturated compounds was investigated in the 77-195°K temperature range. Ethylene, propene, and propyne did not undergo addition reactions, whereas the products obtained from 1,3-butadiene and isoprene were very unstable upon warm-up. The experimentally most amenable system, consisting of isobutylene and nitrosonium nitrate in ethane-propane solution, was studied most extensively. The reactions were conducted at temperatures at which the symmetrical form of N_2O_4 is unreactive toward isobutylene. An unstable solid, believed to be the *cis* dimeric form of isobutylene nitrosonitrate, was isolated. This solid was converted into a thermally unstable liquid product at temperatures above 0°. The chemical and physical characteristics of the latter are consistent with 2-nitratoisobutyraldoxime structure. The role of nitrosonium nitrate in the reactions of N_2O_4 with olefins is discussed.

It has been generally presumed,² on the basis of studies conducted in ether solution,³ that the reactions of dinitrogen tetroxide with olefins occur by free-radical mechanism.



Schoenbrunn and Gardner⁴ studied the oxidation of isobutylene with dinitrogen tetroxide. They isolated some intermediate products (2-nitratoisobutyraldehyde, 2-nitratoisobutyric anhydride, and 2-nitratoisobutyric acid) and obtained good yields of the desired 2-hydroxyisobutyric acid. Significantly, these compounds differed from the products obtained in the analogous reaction in ether solution (1,2-dinitro-2-methylpropane, nitro-t-butyl nitrite, and nitro-t-butyl nitrate).⁵ Schoenbrunn and Gardner concluded^{4a} that in the reactions of olefins with dinitrogen tetroxide the weakly basic solvents not only moderate the oxidizing action of N_2O_4 by complexing, as it had appeared earlier,⁶ but they alter the reaction mechanism. These authors suggested that in the absence of weakly basic solvents the reactions proceed by an ionic mechanism *via* the

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