

Kinetics of aromatic iodination reactions using iodine, diiodine pentoxide and sulfuric acid in acetic acid

2 PERKIN

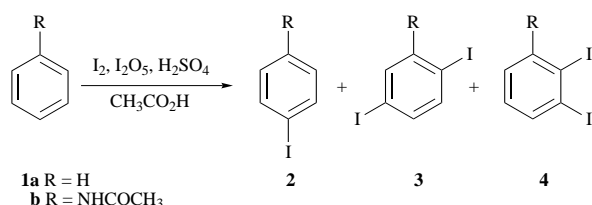
Linda C. Brazdil,* Jill L. Fitch, Carlo J. Cutler, Denise M. Haynik and Eryn R. Ace

Department of Chemistry, John Carroll University, University Heights, OH 44118, USA

Kinetic studies of an aromatic iodination reaction using benzene or acetanilide, iodine, diiodine pentoxide and sulfuric acid in glacial acetic acid have been carried out. The reaction, followed using FT-Raman spectroscopy to monitor the disappearance of the aromatic over time, exhibits fractional order dependence in benzene but first order dependence in acetanilide. The difference in order between the two aromatics indicates that benzene participates in an equilibrium reaction before the rate limiting step of the reaction. This reversible step is proposed to be the reversible formation of a π -complex between adsorbed I_2 and benzene as it adsorbs onto I_2O_5 . Based on the calculated order, acetanilide most likely does not form a π -complex with adsorbed I_2 , rather it reacts from solution to form a σ -complex with activated I_2 on the I_2O_5 surface. In both reactions, it is proposed that the rate limiting step is the formation of the σ -complex.

Introduction

Iodination of aromatic rings is an electrophilic substitution reaction with wide application in organic synthesis, particularly in the synthesis of pharmaceuticals.¹⁻⁶ Like bromine and chlorine, iodine can be polarized to make it more electrophilic. However, elemental iodine is the least electronegative of the three and usually requires the presence of an oxidizing agent before it takes part in aromatic substitution reactions. Soulen and co-workers reported a method for iodinating both activated and deactivated aromatic compounds⁷ that eliminates many of the problems associated with current methods of iodination, particularly problems with heavy metal iodide salt waste.^{1,8-14} This method is shown in Scheme 1.



Scheme 1

In spite of its selectivity toward monoiodination of aromatics other than **1a**,⁷ it appears that both iodine atoms from I_2 are incorporated into the desired products. Based on the yields reported, this must be the case, assuming that no iodine from I_2O_5 is incorporated into the products, an assumption that has yet to be verified. Previous work in our laboratory has shown that when **1a** is iodinated in this manner, **3a** and small amounts of **4a** are produced in addition to **2a**.¹⁵ The amounts of **3a** and **4a** versus **2a** can be regulated by the amount of I_2 added to the reaction mixture.

Since the mechanism of this iodination reaction is not known, we undertook an investigation of its kinetics. Generally, electrophilic aromatic substitution takes place by an attacking electrophile forming a carbocation, or σ -complex, with the aromatic in a rate limiting step. The leaving group is removed and the aromaticity of the ring is restored in a subsequent fast step. The formation of a π -complex prior to σ -complex formation has been proposed for several electrophilic aromatic substitution reactions.^{8,9} Although less common than direct

σ -complex formation, the formation of π -complexes has been observed when aromatics react with I_2 , Br_2 or HCl . In some instances π -complexes can be isolated. However, the π -complex is less stable than the σ -complex and it is hard to prove that it is present in a reaction.

I_2O_5 has been used previously to activate I_2 for electrophilic aromatic substitution. I_2O , I^+ and I_{1+2n}^+ where $n = 1$ or 2 were proposed as intermediates in concentrated H_2SO_4 solutions.¹⁶ The latter intermediate was formed by reaction of I^+ with n molecules of I_2 . These intermediates formed triiodochlorobenzene from chlorobenzene. Iodine that was not used re-formed I_2 . However, scarcely any reaction was observed in dilute H_2SO_4 . In other cases,¹⁷⁻¹⁹ iodination using I_2 and I_2O_5 in methanol occurred on alkyne substituent groups rather than on the aromatic ring itself. In contrast, the current method of electrophilic aromatic substitution occurs selectively with only catalytic amounts of H_2SO_4 .

Because of the importance of aromatic iodination reactions and the ability of the current method to carry out this reaction without the heavy metal iodide wastes often associated with this process, a study was undertaken to understand the mechanism by which this reaction occurs. The kinetics of two aromatics, **1a** and **1b**, were investigated in this study.

Results

The iodination of **1** was followed under various conditions using Raman spectroscopy. A factorial design bracketing the conditions previously described¹⁵ was used to ensure that the kinetics observed were consistent with those under typical synthetic reaction conditions. Table 1 gives the concentrations of reactants used in these experiments. During the course of each reaction, the Raman band at 1000 cm^{-1} for **1** decreased with time in comparison to the acetic acid band at 900 cm^{-1} . Bands associated with **2a** ($1017, 996, 657$ and 266 cm^{-1}), **2b** (1072 and 1594 cm^{-1}), **3a** (1051 and 684 cm^{-1}) and/or **4a** (1045 and 317 cm^{-1}) increased in intensity.

As shown in Table 2, the initial rates for this reaction increase with concentration of **1**. The orders, calculated by comparing the increase in observed rate with increasing concentration of **1** while other concentrations are held constant, are 0.55, 0.70 and 0.85 in **1a** at 323, 333 and 343 K, respectively; the reaction is first order in **1b** at all temperatures studied. Orders in I_2 and

Table 1 Experimental design parameters for iodination reactions with 60 μl H_2SO_4 in 2 ml glacial acetic acid

Condition	[1a]/M (± 0.05)	[1b]/M (± 0.05)	Amt I_2 / g (± 0.02)	Amt I_2O_5 / g (± 0.02)
1	0.50	0.55	0.11	0.15
2	1.50	1.65	0.11	0.15
3	0.50	0.55	0.11	0.44
4	1.50	1.65	0.11	0.44
5	0.50	0.55	0.33	0.15
6	1.50	1.65	0.33	0.15
7	0.50	0.55	0.33	0.44
8	1.50	1.65	0.33	0.44

Table 2 Initial rates and 1 rate coefficients for aromatic iodination reactions

Condition ^a	T/K	Initial rate for 1a/M h ⁻¹ (± 0.01)	k(1a)/ h ⁻¹ (± 0.05)	Initial rate for 1b/M h ⁻¹ (± 0.05)	k(1b)/ h ⁻¹ (± 0.1)
1	323	0.15	0.21	1.44	2.67
2	323	0.25	0.21	4.41	2.67
3	323	0.19	0.28	1.47	2.67
4	323	0.35	0.28	4.40	2.65
5	323	0.19	0.28	1.40	2.64
6	323	0.35	0.28	4.02	2.42
7	323	0.25	0.34	1.60	2.91
8	323	0.44	0.33	4.80	2.91
1	333	0.19	0.27	2.03	3.69
2	333	0.40	0.30	7.07	3.72
3	333	0.23	0.37	2.20	3.63
4	333	0.49	0.37	5.90	3.60
5	333	0.22	0.35	2.04	3.71
6	333	0.46	0.35	6.12	3.71
7	333	0.28	0.45	1.99	3.69
8	333	0.60	0.45	6.12	3.71
1	343	0.20	0.37	2.60	4.91
2	343	0.50	0.37	8.20	5.00
3	343	0.33	0.52	2.54	4.70
4	343	0.75	0.53	8.02	4.15
5	343	0.28	0.50	2.60	4.89
6	343	0.71	0.50	7.40	4.48
7	343	0.35	0.63	2.97	5.50
8	343	0.90	0.64	9.06	5.46

^a Conditions as given in the experimental design described in Table 1.

I_2O_5 could not be calculated from these data since I_2 is not completely dissolved under these conditions and I_2O_5 is insoluble in glacial acetic acid. For this reason reactions were carried out using lower amounts of I_2 that were completely soluble in the reaction mixture. The iodination rates of **1a** under these conditions indicate that the order in I_2 is 0.90 ± 0.05 , as calculated from Table 3. It also was noted that a Raman band at 188 cm^{-1} appeared either in place of or along with the Raman band for iodine at 216 cm^{-1} while the reaction progressed. By changing the amount of H_2SO_4 added to the reaction mixture, the order in H_2SO_4 is calculated to be 0.80 ± 0.05 from the rate data in Table 3.

Linear regressions of $\ln k_1$ vs. $1/T$ for series in which the concentration of **1** changed while the amounts of I_2 and I_2O_5 were held constant in the temperature range 323–343 K were performed. The calculated activation energies from these regressions are thus $27.8 \pm 1.6 \text{ kJ mol}^{-1}$ for **1a** and $28.3 \pm 1.0 \text{ kJ mol}^{-1}$ for **1b**.

Initial rates for the disappearance of **1b** vs. time for three reactions under condition 6 (see Table 1) at 333 K, one in glacial acetic acid, another in [^2H]acetic acid, and a third in [$^2\text{H}_2$]acetic acid, are all 6.12 M h^{-1} . Therefore, there is no kinetic isotope effect for the deuterated solvent in the iodination of **1b**.

When iodination reactions were performed using chloroform in place of acetic acid, no iodinated aromatic products were observed. When small amounts of acetic acid were included in the reaction mixture, iodinated products were formed. How-

Table 3 Initial rates and rate coefficients for **1a** iodination (1.0 M) with changes in I_2 and H_2SO_4 concentrations

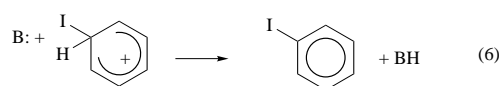
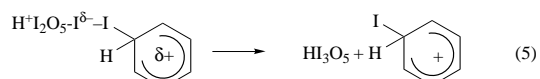
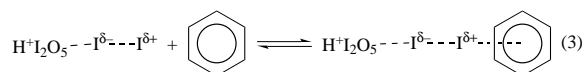
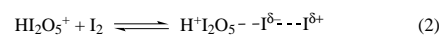
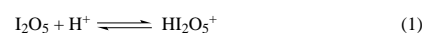
Amt I_2 /g	Amt I_2O_5 /g	Amt H_2SO_4 / μl	Initial rate/M h ⁻¹
0.0510	0.0800	60.0	0.19
0.1000	0.0800	60.0	0.35
0.0275	0.1600	60.0	0.11
0.0500	0.1600	60.0	0.19
0.1013	0.1600	60.0	0.36
0.0275	0.0800	0.0	0.01
0.0275	0.0800	30.0	0.18
0.0275	0.0800	60.0	0.31

ever, their formation occurred at a lower rate than when the reactions were carried out in acetic acid solvent, as indicated by the smaller product yields observed after 24 h.

Because the orders in **1a** are less than one in all of the reactions, the possibility of aromatic adsorption onto I_2O_5 was explored. The straight line dependence observed for the natural log of **1a** adsorbed per gram of I_2O_5 vs. the natural log of **1a** concentration (lines with correlation coefficients >0.99) indicate that adsorption data obey the Freundlich isotherm, an isotherm which describes many systems involving solutes from a liquid solution adsorbing onto a solid adsorbent. Under the same conditions, **1b** does not adsorb onto I_2O_5 .

Discussion

All of the results can be explained according to generally accepted mechanisms of electrophilic aromatic substitution. From the calculated orders, the rate law of the reaction is $\text{rate} = k_{\text{obs}}[\mathbf{1}]^x[\text{I}_2]^{0.90}[\text{H}_2\text{SO}_4]^{0.80}$ where $x = 0.55$ at 323 K, 0.70 at 333 K and 0.85 at 343 K. The fractional orders in **1a**, I_2 and H_2SO_4 indicate that these are probably adsorbed on the surface of I_2O_5 prior to or during the rate limiting step in the reaction, as shown in Scheme 2.

**Scheme 2**

Using a Langmuir–Hinshelwood type mechanism,²⁰ the rate of reaction between adsorbed species is proportional to the concentration of the adsorbed species, not to the concentration of species in solution. This concentration of adsorbed species, θ , is given by $\theta = K[\text{A}]/(1 + K[\text{A}])$, where $[\text{A}]$ is the concentration of species A in solution and K is the equilibrium constant for its adsorption onto a substrate. The presence of $[\text{A}]$ in both the numerator and the denominator leads to observed fractional orders. These equilibria, (1)–(3) are shown in Scheme 2 for acid, I_2 and **1a** adsorption on I_2O_5 , respectively. Freundlich isotherms²⁰ also predict fractional orders for adsorbed species, but do not provide a physical basis for this observation.

Adsorption data indicate that **1a** is adsorbed on I_2O_5 under

reaction conditions. As would be expected, less adsorption occurs at higher temperatures, leading to an increase in the observed order of the reaction in **1a**.

Additionally, reaction of acids with I_2O_5 is known. Specific reactions of H_2SO_4 with I_2O_5 to produce $I_2O_5 \cdot SO_3$ ¹⁶ or $[IO]_2 \cdot SO_4$ ²¹ during this reaction are unlikely since H_2SO_4 can be replaced with phosphotungstic acid in the reaction mixture.²²

Evidence for I_2 - I_2O_5 interaction, as depicted in equilibrium (2) of Scheme 2, is seen in FT-Raman spectra. The shift to lower energy of the I_2 peak during reaction indicates that the I-I bond is still intact, but weakened, as would be expected in an activated molecule. The order in iodine is further support that the I-I bond is intact. If I_2 adsorbed dissociatively, the I-I bond would be broken and the expected order in I_2 would be equal to or less than 0.5 unless this bond breaking is rate limiting. The order in I_2 also would be 0.5 or less if I_2 was involved in a pre-equilibrium in which it dissociated. While reaction with I_2O_5 resulting in a soluble species containing an intact, activated I_2 moiety is possible, it is judged to be less likely since it must react with an adsorbed molecule of **1**.

In iodination reactions previously studied under similar conditions, a first order dependence on I_2 was observed. Intermediates which have been proposed in these systems are HIO , HIO_3 and CH_3CO_2I .²³⁻²⁶ The authors propose that the formation of the activated iodine species is the rate limiting step in these reactions. Indeed, they observed a zero-order dependence in **1** for the reactions, indicating the attack by the activated iodine species on **1** is fast compared with the activation step. Although conditions in the present study are similar to those reported previously, iodine activation clearly is not the rate limiting step since a dependence on **1** is observed. The difference in the oxidizing agent, I_2O_5 vs. peracetic acid, and the heterogeneous nature of the present system are sufficient to change the mechanism of the iodination reaction. A possibility consistent with all of these observations is that I_2O_5 polarizes the I_2 as it adsorbs, making it more electrophilic.

As depicted in Scheme 2, the first step in the reaction is probably the reaction of acid with I_2O_5 , I_2 then is adsorbed onto I_2O_5 associatively, generating an electrophilic iodine species. There are two explanations, compatible with known mechanisms for electrophilic aromatic substitution and consistent with the data, that can describe the mechanism beyond this point. One is that the activated I_2 binds reversibly with **1a** through its delocalized electron cloud to form a π -complex, as shown in equilibrium (3) of Scheme 2. Through further interactions, a σ -complex is formed from the π -complex. The rate limiting step could be σ -complex formation [reaction (4) in Scheme 2] or C-H bond cleavage [reaction (6) in Scheme 2]. If formation of the σ -complex is rate limiting, it may be formed prior to or simultaneously with the breaking of the I-I bond. In the latter case, reactions (4) and (5) of Scheme 2 would be combined. The other explanation is that reversible adsorption of **1a** occurs on a surface site on I_2O_5 unoccupied by I_2 prior to an irreversible step to form a σ -complex. This mechanism does not necessitate the formation of a π -complex. However, the electrophilic nature of the iodine supports the idea of **1a** adsorption on sites containing I_2 . No conclusive evidence for the site of **1a** adsorption has been obtained in this study, although **1a** has been shown to adsorb onto I_2O_5 at 333 K both in the presence and absence of I_2 .

These possibilities are also consistent with the first order dependence in **1b**. Since the activated aromatic system forms a more stable complex than does **1a** on initial attack of the activated I_2 , the reverse reaction for **1b** would be negligible. Additionally, there is no evidence that **1b** adsorbs on the surface of I_2O_5 prior to reaction with activated I_2 . Rather, the observed first order dependence in **1b** indicates reaction from solution with adsorbed I_2 to form a σ -complex in a rate limiting step. Thus reactions (3) and (4) in Scheme 2 would be combined if **1b** replaced **1a** in this scheme. It is possible that a π -complex [equi-

librium (3) in Scheme 2] is formed irreversibly with **1b**; this would necessitate a single arrow replacing the equilibrium arrows for this step when **1b** is involved. Once formed the π -complex would react rapidly to form the σ -complex. The reaction still would have a first order dependence in **1b**. As with **1a** above, the σ -complex may be formed prior to or simultaneously with the breaking of the I-I bond.

When acetic acid was replaced with chloroform in these reactions, no iodinated aromatic products were observed. Therefore, acetic acid must play a role in the reaction. However, there is no change in the rate of reaction when acetic acid is replaced with [2H]acetic acid or [2H_4]acetic acid. This indicates that the proton in acetic acid does not activate I_2 in this system. If, however, I_2 is interacting with the oxygen in the acetic acid molecule, no effect of deuterium would be expected. During experiments conducted using deuterated solvents, the Raman band corresponding to **1b** at 1005 cm^{-1} was shifted to 1011 cm^{-1} . This indicates exchange of H and D between the solvent and **1b**. This type of exchange is not surprising under conditions conducive to electrophilic aromatic substitution.²⁷ However, there is an excess of deuterated solvent in the reaction when compared to **1b** (0.035 mol deuterated solvent *versus* 0.0033 mol **1b**) so the number of protons replacing deuterium on acetic acid is not enough to account for the lack of an observed kinetic isotope effect.

While it is possible that I_2 reacts with the oxygen in acetic acid to form an intermediate, it appears that I_2O_5 activates I_2 in this system, particularly since no reaction is seen without I_2O_5 . It is unclear from the present study what the exact role of acetic acid is. It probably stabilizes the transition state of the π -complex or facilitates desorption of **2** from the I_2O_5 surface. Diacetate compounds of **2** are known²¹ and, while their role here is unclear, it appears that they may play a vital role in the formation of iodinated aromatics.

With the formation of the iodinated products, I_2O_5 is left with an iodine atom adsorbed, and H^+ is regenerated. The I_2O_5 with H^+ and iodine atoms attached probably reacts with another equivalent of **1** or with an aromatic which is already monoiodinated to produce diiodinated products. This would account for formation of **3a** and **4a**. It is consistent with Soulen and co-workers' report of incorporation of both iodine atoms from I_2 ⁷ and the lack of iodide waste in the present study. The acid catalyst that is regenerated then can react with I_2O_5 and catalyze further reaction. No detailed information about these steps is given from the current study.

Experimental

Materials

All chemicals were A.C.S. reagent grade unless otherwise noted. **1a**, I_2O_5 (98+%), [2H]acetic acid and [2H_4]acetic acid (both 98% D) were obtained from Aldrich. I_2O_5 was stored in a desiccator due to its hygroscopic nature. **1b** (A.C.S. reagent grade) was obtained from J. T. Baker. H_2SO_4 and glacial acetic acid were obtained from Fisher Scientific, and U.S.P. I_2 crystals were obtained from Malinckrodt. All chemicals were used without further purification.

Iodination reactions

Generally, I_2 , I_2O_5 and H_2SO_4 were added to glacial acetic acid. The mixture was equilibrated to reaction temperature. After approximately 5 min, **1** was also added and the reaction proceeded.

For kinetic experiments, the disappearance of **1** was followed directly using FT-Raman spectroscopy. Spectra were collected using 180° collection optics, 500 mW power, 4 cm^{-1} resolution, a scan range of $100\text{--}4000\text{ cm}^{-1}$, and 10 scans per spectrum. Low wattage was needed in order to avoid localized heating of the dark colored solution. A heated cell was designed for per-

forming reactions in the Raman spectrometer. The cell holds a quartz cuvette with a 1.0 cm path length and a Teflon cap. Heating is achieved with a heating block positioned behind the cuvette and regulated electronically. Heat was dispersed by the use of a water jacket. This system maintains temperature of ± 0.5 K.

For **1a** reactions, spectra were obtained every 1 to 3 min for the first 10–15 min and every 5 min thereafter to 45 min. For **1b** reactions, spectra were obtained every 1 to 3 min for a total of 20 min. The reaction mixture was stirred after each spectrum was obtained to ensure good contact between the I_2O_5 and the rest of the reactants. The mixture was not exposed to the laser between scans.

Both aromatics, **1**, have bands in the Raman region which are well separated from the solvent and product peaks and are strong enough to follow throughout the reaction. The strongest and most defined band for **1** is at approximately 1000 cm^{-1} (1000 for **1a** and 1005 cm^{-1} for **1b**). This band corresponds to a C–C ring vibration in both aromatics. The height of this peak was normalized against an acetic acid peak at 900 cm^{-1} and compared to calibration curves in order to calculate the concentration of **1** present at any time in the reaction. The Raman peaks associated with **1** and acetic acid were shifted during reactions using deuterated solvent. Therefore, the aromatic peak at 1011 cm^{-1} was normalized against an acetic acid peak at 866 cm^{-1} for [2H]acetic acid, and at 805 cm^{-1} for [2H_4]acetic acid.

Reactions of **1a** were carried out on a larger scale in round bottom flasks as described previously.¹⁵ Mixtures of **1a** (4.3 g, 1.1 M) in 50 ml solvent (glacial acetic acid, chloroform or a mixture of 45 ml acetic acid and 5 ml chloroform), 14.0 g I_2 , 7.3 g I_2O_5 and 1.5 ml H_2SO_4 were allowed to react for 24 h. After the mixtures were cooled to room temperature, 100 ml distilled water was added to dissolve I_2O_5 . The resulting mixtures were filtered. This separated **3a** (in acetic acid: 8.35 g, 46%; in acetic acid–chloroform mix: 1.56 g, 8.6%; in chloroform: none observed) from the mixture. **4a** (in acetic acid: 8.0%; in acetic acid–chloroform mix, 1.5%; in chloroform: none observed) and **2a** (in acetic acid: 45%; in acetic acid–chloroform mix, 8.0%; in chloroform: none observed) formed an oily layer which was separated and washed with an aqueous solution of KI and $Na_2S_2O_3$ and dried over $CaCl_2$.^{15,25} The products were weighed and then dissolved in acetic acid and analyzed by Raman and 1H NMR spectroscopy to determine the amount of each present. All NMR spectra matched those of authentic samples: δ_H (300 MHz; CD_3CO_2D) **3a** 7.46 (4 H, s, I- C_6H_4 -I); **4a** 7.05 [2 H, d, C(4)H], 7.89 [2 H, d, C(3)H]; **2a** 7.08 [2 H, t, C(2)H], 7.31 [1 H, t, C(4)H], 7.73 [2 H, d, C(3)H].

In order to determine whether nitrogen blanketing was necessary, comparative studies were performed in which some **1b** iodination experiments were conducted under flowing nitrogen with analogous reactions performed using only an initial blanket of nitrogen or without any nitrogen blanket. Analysis of crude products indicated approximately 65% yield of **2b** in all cases; only trace amounts of 2-iodoacetanilide were observed. NMR analysis confirmed product identification: δ_H (300 MHz; CD_3CO_2D) **2b** 7.37 [2 H, d, C(2)H], 7.63 [2 H, d, C(3)H]. This implied that the reactions performed under all three conditions were comparable. Therefore, further reactions were not blanketed in nitrogen.

Adsorption studies

Adsorption studies were carried out by equilibrating mixtures

of **1**, glacial acetic acid and H_2SO_4 to 333 K in a water bath. Raman spectra were collected to determine the initial concentrations of **1** present. Concentrations were calculated as described above. I_2O_5 then was added to each solution. The solutions were kept at 333 K and shaken every 5 min. After 1 h, the liquid was separated from the I_2O_5 and Raman spectra were collected. The amount of **1** adsorbed onto I_2O_5 was calculated from the difference in concentrations between the solutions before and after contact with I_2O_5 .

Acknowledgements

This material is based upon work supported by the National Science Foundation under Grant Number CHE-9520439. The authors are grateful for the support provided by this organization. Two of the authors (J. L. F. and C. J. C.) also are grateful for BP America Summer Fellowships.

References

- 1 A. Bachi, F. Foubelo and M. Yus, *Tetrahedron*, 1994, **50**, 5139.
- 2 G. A. Olah, Q. Wang, G. Sanford and G. K. S. Prakash, *J. Org. Chem.*, 1993, **58**, 3194.
- 3 R. C. Larock and E. K. Yum, *J. Am. Chem. Soc.*, 1991, **113**, 6689.
- 4 R. C. Larock and N. H. Lee, *J. Org. Chem.*, 1991, **56**, 6253.
- 5 E. C. Taylor and G. S. K. Wong, *J. Org. Chem.*, 1989, **54**, 3618.
- 6 W. C. Eckelman, H. R. Adams and C. H. Paik, *Int. J. Nucl. Med. Biol.*, 1984, **11**, 163.
- 7 A. Keyes, D. R. Johnson and R. L. Soulen, presented at the 208th American Chemical Society National Meeting, Washington, DC, 1994, Abstract 72.
- 8 C. J. Galli and S. D. Giammarino, *J. Chem. Soc., Perkin Trans. 2*, 1994, 1261.
- 9 C. J. Galli, *J. Org. Chem.*, 1991, **56**, 3238.
- 10 E. B. Merkushev, *Synthesis*, 1988, 923.
- 11 R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, 1956, **78**, 5623.
- 12 C. A. Horiuchi and J. Y. Satoh, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 2691.
- 13 M. Kodamari, H. Satoh and S. Yoshitomi, *J. Org. Chem.*, 1988, **53**, 2093.
- 14 T. Okamoto, T. Kakinami, T. Nishimura, I. Hermawan and S. Kajigaeshi, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 1731.
- 15 L. C. Brazdil and C. J. Cutler, *J. Org. Chem.*, 1996, **61**, 9621.
- 16 I. Masson, *J. Chem. Soc.*, 1938, 1708.
- 17 J. J. Janas, E. T. Asirvatham and E. McNelis, *Oxid. Commun.*, 1985, **8**, 65.
- 18 M. J. Cohen and E. McNelis, *J. Org. Chem.*, 1984, **49**, 515.
- 19 G. Gebeyehu and E. McNelis, *J. Org. Chem.*, 1980, **45**, 4280.
- 20 K. J. Laidler, *Chemical Kinetics*, Harper Collins, New York, 3rd edn., 1987, pp. 230–234, 248–252.
- 21 A. F. Wells, *Structural Inorganic Chemistry*, Clarendon Press, Oxford, 5th edn., 1984, pp. 386, 401.
- 22 D. M. Haynik and L. C. Bradzil, presented at the Cleveland Section American Chemical Society Meeting in Miniature, Cleveland, March, 1997.
- 23 Y. Ogata and K. Aoki, *J. Am. Chem. Soc.*, 1968, **90**, 6187.
- 24 Y. Ogata and K. Nakajima, *Tetrahedron*, 1964, **20**, 43.
- 25 Y. Ogata and K. Nakajima, *Tetrahedron*, 1964, **20**, 2751.
- 26 Y. Ogata and I. Urasaki, *J. Chem. Soc. C*, 1970, 1689.
- 27 L. Melander, *Isotope Effects on Reaction Rates*, The Ronald Press Co., New York, 1960, p. 124.

Paper 7/06735F

Received 8th September 1997

Accepted 17th December 1997