

# Initiation of Cationic Polymerization of Cyclic Ethers by Redox Radical-Chain Reactions of Onium Salts<sup>1</sup>

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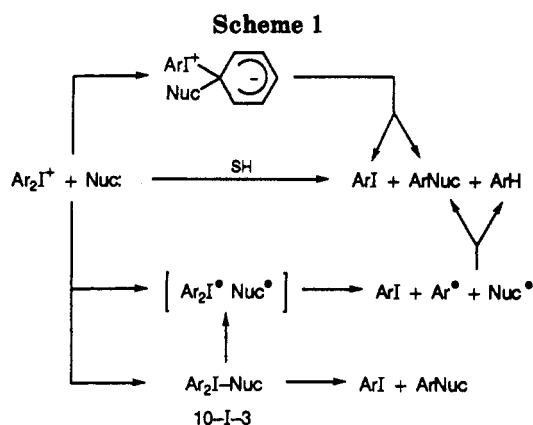
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Redox radical-chain reactions of diaryliodonium halides ( $\text{Ar}_2\text{I}^+\text{X}^-$ ) with tetrahydrofuran (THF) and 1,3-dioxolane to give arenes ( $\text{ArH}$ ) and iodoarenes ( $\text{ArI}$ ) are reported. When the reactions are initiated by irradiation at 313 nm, the quantum yield for the formation of iodoarene is substantially greater than 1 ( $\Phi \approx 2-20$ ). Nonphotochemical radical initiators give the same reaction, showing that the photochemical step is simply an initiation step. The key propagation step in these reactions is a single-electron reduction of the onium salts by ether-derived radicals. The photoinitiated reaction with THF follows zero-order kinetics, showing that termination does not compete with electron transfer. In addition, the same nonphotochemical conditions that give radical-chain reduction of the diaryliodonium halides give rapid cationic polymerization of the ethers when the iodonium hexafluorophosphates are used. These observations establish the connection between the redox chemistry of the iodonium salt and the cationic polymerization of the ethers. The polymerization of THF by iodonium salt in the presence of free radicals is accelerated by the addition of trimethyl phosphite (TMP). Furthermore, triarylsulfonium salts will initiate polymerization of THF in the presence of TMP and radical sources. Therefore, redox-chain reduction of these onium salts by TMP can also initiate cationic polymerization of the cyclic ethers.

## Introduction

The chemistry of iodonium salts has been the subject of much recent interest, both for its increasing use in organic synthesis<sup>2</sup> and for mechanistic reasons.<sup>3</sup> The literature supports the conclusion that iodonium chemistry can be messy, with ionic and radical processes often closely balanced and in competition with each other.<sup>4</sup> Reactions of iodonium salts with nucleophiles, for example, give collections of products, rationalized by a variety of proposed mechanisms (Scheme 1) including an  $\text{S}_{\text{N}}\text{Ar}$  process,<sup>5</sup> attack on iodine to give a 10-I-3 intermediate with subsequent ligand coupling<sup>6</sup> or homolysis,<sup>7</sup> and



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(1) Results presented, in part, at the 4th International Symposium on Organic Free Radicals, University of St. Andrews, London, 1984 (Abstract: Nalli, T.; Kampmeier, J. A. *Abstracts of Plenary Lectures, Contributed Papers, and Posters*, Abstract O.30) and at the 205th National Meeting of the American Chemical Society, Denver, CO, April 1993 (Abstract: Kampmeier, J. A.; Nalli, T. W. *Book of Abstracts*, ORGN 340).

(2) For reviews, see: (a) Moriarty, R. M.; Vaid, R. K.; Koser, G. F. *Synlett* 1990, 365-383. (b) Moriarty, R. M.; Vaid, R. K. *Synthesis* 1990, 431-437. (c) Moriarty, R. M.; Prakash, O. *Acc. Chem. Res.* 1986, 19, 244-250. (d) Varvoglis, A. *Synthesis* 1984, 709-726.

(3) See, for example: (a) Dektar, J. L.; Hacker, N. P. *J. Org. Chem.* 1990, 55, 639-647. (b) Devoe, R. J.; Sahyun, M. R. V.; Serpone, N.; Sharma, D. K. *Can. J. Chem.* 1987, 65, 2342-2349.

(4) See, for example: (a) Lubinkowski, J. J.; Arrieche, C. G.; McEwen, W. E. *J. Org. Chem.* 1980, 45, 2076-2079. (b) Lubinkowski, J. J.; Gomez, M.; Calderon, J. L.; McEwen, W. E. *Ibid.* 1978, 43, 2432-2435. (c) Lubinkowski, J. J.; Knapczyk, J. W.; Calderon, J. L.; Petit, L. R.; McEwen, W. E. *Ibid.* 1975, 40, 3010-3014. (d) Knapczyk, J. W.; Lubinkowski, J. J.; McEwen, W. E. *Tetrahedron Lett.* 1972, 3739-3742. (e) McEwen, W. E.; Lubinkowski, J. J.; Knapczyk, J. W. *Ibid.* 1972, 3301-3304. (f) Beringer, F. M.; Falk, R. A. *J. Chem. Soc.* 1964, 4442-4451 (g) Beringer, F. M.; Gindler, E. M.; Rapoport, M.; Taylor, R. J. *J. Am. Chem. Soc.* 1959, 81, 351-361. (h) Davidson, R. S.; Goodin, J. W. *Eur. Polym. J.* 1982, 18, 589-595.

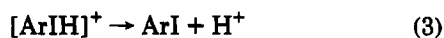
(5) See, for example: (a) Beringer, F. M.; Mausner, M. *J. Am. Chem. Soc.* 1958, 80, 4535-4536. (b) Beringer, F. M.; Briery, A.; Drexler, M.; Gindler, E. M.; Lumpkin, C. C. *J. Am. Chem. Soc.* 1958, 80, 2708-2712. (c) Yamada, Y.; Kashima, K.; Okawara, M. *Bull. Chem. Soc. Jpn.* 1974, 47, 3179-3180. (d) Lancer, K. M.; Wiegand, G. H. *J. Org. Chem.* 1976, 41, 3360-3364.

reductive, nonchain radical processes.<sup>8</sup> In addition, a variety of redox, radical-chain possibilities has been identified.<sup>9</sup>

Crivello and Lam<sup>10</sup> were the first to report that diaryliodonium cations with nonnucleophilic counteranions (e.g.,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ) are efficient photoinitiators of cationic polymerization of cyclic ethers such as tetrahydrofuran (THF). These authors have presented arguments in favor of a nonradical, nonchain mechanism for photoinitiation of polymerization involving iodoarene radical cations ( $\text{ArI}^+$ ) and protons as the key species (eqs 1-4). This mechanism is based, in part, on the products and quantum yield of photolysis of diaryliodonium fluoroborate in acetonitrile ( $\Phi = 0.2$ ).<sup>10a</sup>

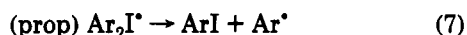
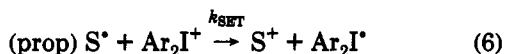
(6) See ref 4d. Also see: (a) Zefirov, N. S.; Koz'min, A. S.; Kaumov, T.; Potekhin, K. A.; Sorokin, V. D.; Brel, V. K.; Abramkin, E. V.; Struchkov, Y. T.; Zhdankin, V. V.; Stang, P. J. *J. Org. Chem.* 1992, 57, 2433-2437. (b) Lyalin, V. V.; Orda, V. V.; Alekseeva, L. A.; Yagupol'skii, L. M. *Zh. Org. Khim.* 1971, 7, 1473-1478. (c) Yagupol'skii, L. M.; Maletina, I. I.; Kondratenko, N. V.; Orda, V. V. *Synthesis* 1978, 835-837. (d) Umamoto, T.; Kuriu, Y.; *Tetrahedron Lett.* 1981, 5197-5200. (e) Umamoto, T.; Miyano, O. *Bull. Chem. Soc. Jpn.* 1984, 57, 3361-3362. (f) Moriarty, R. M.; Epa, W. R.; Penmasta, R.; Awasthi, A. K. *Tetrahedron Lett.* 1989, 667-670.

(7) Proposed as an initiation step in refs 4c-e. Also see: (a) Foster, D. L. D.; Hobbs, P. D.; Magnus, P. D. *Tetrahedron Lett.* 1972, 4793-4794. (b) Irving, H.; Reid, R. W. *J. Chem. Soc.* 1960, 2078-2081.



(SH  $\equiv$  cyclic ether monomer)

An alternative radical-chain mechanism (eqs 1, 5, 6, 7, and 8) was proposed by Ledwith<sup>11</sup> with support provided by a kinetic analysis of the living polymerization and by polymerization experiments employing thermal radical sources. However, the underlying iodonium chemistry was not directly revealed by this work. We explored this chemistry by studying the behavior of iodonium halides in polymerizable solvents; the nucleophilic halide ions provided a means to prevent polymerization without altering the fundamental iodonium chemistry.



### Results and Discussion

The decomposition of 4,4'-di-*tert*-butyldiphenyliodonium chloride (1) was examined in cationically polymerizable solvents, 1,3-dioxolane and THF (Tables 1 and 2). Thermal decomposition of 1 in refluxing dioxolane (temp = 75 °C) gave 4-*tert*-butyliodobenzene (ArI) and 4-*tert*-butylchlorobenzene (ArCl) in equal amounts (expt 2, Table 1), an apparent ionic  $\text{S}_{\text{N}}\text{Ar}$  reaction. In contrast, the photochemical decomposition of 1 at room temperature gave only traces of chloroarene. The apparent free-radical product, *tert*-butylbenzene (ArH) was formed instead (expts 4, 6, and 8, Table 1). The photochemical reaction has a quantum yield of  $14 \pm 2$  at 313 nm in dioxolane<sup>12,13</sup> (expt 22, Table 2), indicating a chain mechanism (eqs 1, 5, 6, and 7) for the decomposition of the iodonium salt.

The same radical-chain reaction can be initiated by the thermal decomposition of di-*tert*-butyl peroxalate (DBPO)

(8) Reference 4f. Also see: (a) Singh, P. R.; Khanna, R. K. *Tetrahedron Lett.* 1982, 23, 5355–5358. (b) Tanner, D. D.; Reed, D. W.; Setiloane, B. P. *J. Am. Chem. Soc.* 1982, 104, 3917–3923. (c) Beringer, F. M.; Galton, S. A.; Huang, S. J. *J. Am. Chem. Soc.* 1962, 84, 2819–2823. (d) Sandin, R. B.; Brown, R. K. *J. Am. Chem. Soc.* 1947, 69, 2253–2254. (e) Levit, A. F.; Kalibabchuk; Gragerov, I. P. *Dokl. Akad. Nauk SSSR* 1971, 199, 1325–1327. (f) Bilevich, K. A.; Bubnov, N. N.; Ioffe, N. T.; Kalinkin, M. I.; Okhlobystin, O. Y.; Petrovskii, P. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1971, 1814–1815. (g) Colquhoun, H. M. *J. Chem. Res., Synop.* 1981, 275.

(9) See refs 4a–e, g. Also see: (a) Ptitsyna, O. A.; Pudeeva, M. E.; Reutov, O. A. *Dokl. Akad. Nauk SSSR* 1966, 168, 595–598; (b) 1965, 165, 838–841. (c) Baumann, H.; Timpe, H. *J. Z. Chem.* 1984, 24, 18–20. (d) Kampmeier, J. A.; Nalli, T. W. *J. Org. Chem.* 1993, 58, 943–949. (e) Nalli, T. W. Ph.D. Dissertation, University of Rochester, 1987.

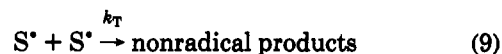
(10) (a) Crivello, J. V.; Lam, J. H. W. *Macromolecules* 1977, 10, 1307–1315. (b) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Symp.* 1976, 56, 383–395. (c) Crivello, J. V. *CHEMTECH* 1980, 624–628. (d) Crivello, J. V. *Adv. Polym. Sci.* 1984, 62, 1–48. (e) Crivello, J. V. *J. Coatings Tech.* 1991, 63, 35–38.

(11) (a) Ledwith, A. *Makromol. Chem., Suppl.* 1979, 3, 348–358. (b) Ledwith, A. *Polymer* 1978, 19, 1217–1219. (c) Abdul-Rasoul, f. A. M.; Ledwith, A.; Yagci, Y. *Ibid.* 1978, 19, 1219–1222. (d) Ledwith, A. *Pure Appl. Chem.* 1975, 51, 159–171.

(expts 9, 10, and 13, Table 1) or AIBN (expt 1, Table 1), by visible light irradiation of phenylazoisobutyronitrile (PAIBN =  $\text{PhN}=\text{NC}(\text{CH}_3)_2\text{CN}$ ,  $\lambda_{\text{max}} = 395 \text{ nm}$ ) (expts 15, 17, 19, and 21, Table 1), and, rather inefficiently, by visible light itself (expts 12, 16, and 18, Table 1). As observed previously by McEwen and co-workers,<sup>4b,c</sup> the rates of the ionic and radical-chain processes are closely balanced. This is demonstrated in our work by the fact that addition of 0.1 equiv of AIBN to the thermal reaction (temp = 75 °C) led to the formation of *tert*-butylbenzene at the expense (but not to the exclusion) of the chloroarene (expt 1, Table 1). Nevertheless, the radical process is cleanly separated from the thermally activated ionic process by simply working at room temperature. The ability of DBPO to initiate the reaction under nonphotochemical conditions clearly indicates that the role of light in the photochemical reaction is simply as a source of free radicals, i.e., the photochemical step is simply an initiation step for a free-radical chain reaction.

The quantum yield ( $\Phi_{313} = 14 \pm 2$ , expt 22, Table 2) that we measured for the formation of 4-*tert*-butyliodobenzene from iodonium salt 1 in 1,3-dioxolane contrasts dramatically with the value previously reported for the photolysis of 1 in acetonitrile,  $\Phi_{313} = 0.22$ .<sup>10a,14</sup> The redox chain requires that the solvent act as a hydrogen atom donor and that the derived solvent radical act as a reductant for the iodonium salt. Cationically polymerizable monomers such as THF and dioxolane fulfill these requirements. Acetonitrile, however, is both a poorer H-donor<sup>15,16</sup> and gives a derived radical,  $\text{NCCH}_2^{\bullet}$ , that is a poorer reductant than the ether-derived radicals.<sup>17</sup> Since the quantum yield in acetonitrile reflects the efficiency of primary photolysis of iodonium salt, it is reasonable to assume that this value approximates the efficiency of initiation in dioxolane. The kinetic chain length for the decomposition of iodonium salt in dioxolane is, therefore, approximately 70.<sup>18</sup>

The photolysis of iodonium salt 1 in THF under continuous illumination at 313 nm follows zero-order kinetics over essentially the full course of the reaction (Figure 1 and expt 40, Table 2). This observation rules out a mechanism (e.g., eqs 1, 5, 6, 7, and 9) that involves self termination of solvent-derived radicals (eq 9) in



competition with electron transfer (eq 6). Therefore, the rate of electron transfer from the tetrahydrofuryl radical to 1 is faster (conservatively, at least 10-fold) than its bimolecular termination (eq 10).

$$\frac{k_{\text{SET}}[\text{THF}^{\bullet}][\text{Ar}_2\text{I}^+]}{2k_{\text{T}}[\text{THF}^{\bullet}]^2} > 10 \quad (10)$$

Assuming that the termination step does compete, steady-state treatment gives an expression for  $[\text{THF}^{\bullet}]$  and leads to eq 11.

(12) Quantum yield for production of ArI from 1 (0.05 M) at low conversion (<15%) measured using the benzophenone-benzhydrol actinometer.<sup>13</sup> See Experimental Section.

(13) Moore, W. M.; Hammond, G. S.; Foss, R. P. *J. Am. Chem. Soc.* 1961, 83, 2789–2794.

(14) Quantum yield for production of ArI from 1 (0.3 M) at low conversion (<10%) measured using a uranyl oxalate actinometer.<sup>10a</sup>

Table 1. Initiation of Solvent-Mediated Radical-Chain Reduction of 4,4'-Di-*tert*-butyldiphenyliodonium Chloride (1) by Common Radical Sources

expt	solvent	[1], mM	initiator (equiv) <sup>b</sup>	method <sup>c</sup>	time, h	yields, <sup>a</sup> %			
						ArI	ArH	ArCl	HCO <sub>2</sub> C <sub>2</sub> H <sub>4</sub> Cl
1	dioxolane	22	AIBN (0.10)	75 °C	7	97	60	32	7
2	dioxolane	43	none	75 °C	44	101	nd	96	nd
3	dioxolane	20	AIBN (0.12)	Hg arc <sup>d</sup>	7.3	93	93	≈1	7
4	dioxolane	26	none	Hg arc <sup>d</sup>	7.3	92	75	≈1	2
5	THF	15	AIBN (0.16)	Hg arc <sup>d</sup>	31	104	98	nd	nd
6	THF	22	none	Hg arc <sup>d</sup>	48	36	33	≈1	nd
7	dioxolane	26	AIBN (0.10)	sunlamp <sup>e</sup>	1.5	82	81	≈1	30
8	dioxolane	23	none	sunlamp <sup>e</sup>	1.5	91	91	≈1	34
9	dioxolane	19	DBPO (0.02)	dark <sup>f</sup>	22	21	22	nd	nd
					48	48	50	nd	nd
10	dioxolane	18	DBPO (0.20)	dark <sup>f</sup>	22	73	71	nd	3
					48	95	98	nd	6
11	dioxolane	23	none	dark <sup>f</sup>	18	nd	nd	nd	nd
12	dioxolane	26	none	ambient <sup>g</sup>	44	11	10	≈1	nd
13	THF	27	DBPO (0.06)	dark <sup>f</sup>	45	29	24	nd	nd
14	THF	27	none	dark <sup>f</sup>	99	nd	nd	nd	nd
15	dioxolane	53	PAIBN (0.15)	floodlamp <sup>h</sup>	26	23	22	nd	nd
16	dioxolane	54	none	floodlamp <sup>h</sup>	26	2	2	nd	nd
17	THF	55	PAIBN (0.17)	floodlamp <sup>h</sup>	26	16	18	nd	nd
18	THF	57	none	floodlamp <sup>h</sup>	26	2	≈1	nd	nd
19	dioxolane	46	PAIBN (0.13)	<i>hν</i> > 395 nm <sup>i</sup>	3	28	31	nd	nd
20	1,4-dioxane	46	PAIBN (0.13)	<i>hν</i> > 395 nm <sup>i</sup>	3	4	≈1	nd	nd
21	THF	48	PAIBN (0.13)	<i>hν</i> > 395 nm <sup>i</sup>	3	15	20	nd	nd

<sup>a</sup> Percent yield based on [1] determined by GC; nd means not detected (limit of detection ≈1%), na means peak was detected but not quantitated. <sup>b</sup> Initiator used; AIBN = azobis(isobutyronitrile), DBPO = di-*tert*-butyl peroxalate, PAIBN = phenylazoisobutyronitrile. Equivalents are calculated on the basis of [1]. <sup>c</sup> Reactions were run at room temperature unless otherwise indicated. <sup>d</sup> Broad-band irradiation with an Hg arc. <sup>e</sup> Irradiation with a 275-W sunlamp. <sup>f</sup> Reaction vessel was wrapped with aluminum foil. <sup>g</sup> Reaction vessel was not shielded from room lights. <sup>h</sup> Irradiation with a 200-W floodlamp and NaNO<sub>2</sub> (aq) filter solution. <sup>i</sup> Irradiation with an Hg arc and NaNO<sub>2</sub> (aq) filter solution.

$$\frac{k_{\text{SET}}[\text{Ar}_2\text{I}^+]}{(2k_{\text{T}}I_0\Phi_i)^{1/2}} > 10 \quad (11)$$

Using the quantum yield for photolysis of 1 in CH<sub>3</sub>CN ( $\Phi_{313} = 0.2$ ) for the efficiency of initiation ( $\Phi_i$ ), the light intensity measured using the benzophenone-benzhydrol actinometer ( $I_0 = 2.3 \times 10^{-5}$  einstein s<sup>-1</sup> L<sup>-1</sup>), the diffusion-controlled termination rate constant for radical coupling ( $k_{\text{T}} = 1.5 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>),<sup>19,20</sup> and the mean iodonium concentration during the photolysis ( $[\text{Ar}_2\text{I}^+] = 0.015$  M), a lower limit on the rate constant for electron transfer from tetrahydrofuryl radical to iodonium,  $k_{\text{SET}} > 8 \times 10^5$  M<sup>-1</sup> s<sup>-1</sup>, can be extracted from eq 11. It is probable that electron transfer from THF<sup>•</sup> to iodonium salt is actually much faster, in the manner of similar electron transfers

(15) Phenyl radical abstracts hydrogen from acetonitrile with the rate constant  $k_{\text{MeCN}} = 1.0 \times 10^6$  M<sup>-1</sup> s<sup>-1</sup>. This is ca. 50 times less than the rate constant for hydrogen donation by THF,  $k_{\text{THF}} = 4.8 \times 10^6$  M<sup>-1</sup> s<sup>-1</sup>. See ref 16.

(16) Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* 1983, 105, 3609–3614.

(17) Oxidation of ether derived radicals gives relatively stable oxonium ions. Oxidation of NCCH<sub>2</sub> gives a substantially less stable carbocation, NCCH<sub>2</sub><sup>+</sup>.

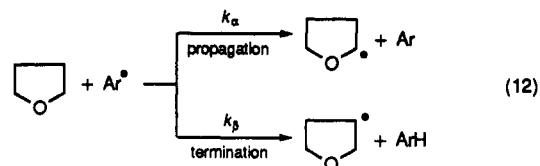
(18) Alternatively, if Dektar and Hacker's<sup>24</sup> recently reported quantum yield for production of 4-iodotoluene from di-*p*-tolyliodonium hexafluorophosphate in CH<sub>3</sub>CN,  $\Phi_{254} = 0.32$ , is viewed as a better approximation of  $\Phi_{\text{init}}$ , then the chain length would be ca. 45.

(19) Calculated for THF from  $2k_{\text{T}} = 8000\pi\sigma dDN$  with  $\sigma$  (spin statistical correction) =  $1/4$  and  $N$  = Avogadro constant.<sup>20a</sup> The reaction diameter,  $d \approx 0.261$  nm, is calculated using a simple volume increment method<sup>20b</sup> for THF. The diffusion coefficient,  $D \approx 1.49 \times 10^6$  cm<sup>2</sup> s<sup>-1</sup>, is calculated from the Stokes-Einstein equation;  $D = kT/6\pi\eta r_{\text{vd}}$  using the viscosity of THF,  $\eta = 0.55$  mPa s.<sup>20c</sup> The result,  $k_{\text{T}} = 1.5 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>, has been confirmed experimentally<sup>20d,e</sup> and has been used previously as a kinetic reference point for measurement of rates of both dioxolanyl and THF radicals.<sup>20d</sup>

(20) (a) Claridge, R. F. C.; Fischer, H. *J. Phys. Chem.* 1983, 87, 1960–1967. (b) Edward, J. T. *J. Chem. Educ.* 1970, 47, 261–270. (c) *Handbook of Chemistry and Physics*, 71st ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1990; p 8-44. (d) Gilbert, B. C.; Norman, R. O. C.; Sealy, R. C. *J. Chem. Soc., Perkin Trans. 2* 1974, 824–830. (e) Henning, P. *Chem. Phys.* 1976, 15, 115–129.

from  $\alpha$ -hydroxyalkyl radicals to arenediazonium salts ( $k_{\text{SET}} = 2\text{--}5 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>)<sup>21</sup> and from phosphoranyl radicals to iodonium ( $k_{\text{SET}} \approx 4 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>).<sup>9d</sup>

Since eq 9 is not a kinetically significant termination step in THF, a different termination step must be postulated. We think it likely that termination occurs through hydrogen abstraction by aryl radical from the  $\beta$  position on THF (eq 12). Steady-state treatment of this



mechanism (eqs 1, 6, 7, and 12) gives eq 13 and predicts the observed zero-order behavior and, perhaps more interestingly, a kinetic chain length that is equal to the relative rates of  $\alpha$ - and  $\beta$ -hydrogen abstraction ( $k_a/k_b$ ). Equation 12 also makes good chemical sense; the hydrogen

$$\frac{d[\text{ArI}]}{dt} = \frac{k_a}{k_b}(I_0\Phi_i) \quad (13)$$

abstraction by an aryl radical is neither expected to be 100% selective for the  $\alpha$  position nor is the  $\beta$ -tetrahydrofuryl radical expected to function as a reductant for iodonium salt. Furthermore, the chain length of the photolysis of iodonium in THF is ca. 10 (expts 33, 35, and 40, Table 2), seemingly a very reasonable value for  $k_a/k_b$ .<sup>22,23</sup>

(21) Packer, J. E.; Monig, J.; Dobson, B. C. *Aust. J. Chem.* 1981, 34, 1433–1441.

Table 2. Quantum Yields ( $\Phi$ ) of Photolysis at 313 nm of 4,4'-Di-*tert*-butyldiphenyliodonium Salts 1<sup>a</sup>

expt	solvent	[1], mM	anion	intensity, <sup>b</sup> einstein s <sup>-1</sup> L <sup>-1</sup>	time, s	ArI, % yield <sup>c</sup>	$\Phi^d$
22 <sup>e</sup>	dioxolane	47	Cl <sup>-</sup>	$1.5 \times 10^{-6}$	300	14	14
23	dioxolane	58	Cl <sup>-</sup>	$2.3 \times 10^{-6}$	540	53	2.5
24	dioxolane	83	Cl <sup>-</sup>	$2.3 \times 10^{-6}$	360	39	3.9
25	dioxolane	44	PhCO <sub>2</sub> <sup>-</sup>	$2.3 \times 10^{-6}$	360	76	4.0
26	dioxolane	83	PhCO <sub>2</sub> <sup>-</sup>	$2.3 \times 10^{-6}$	540	77	5.1
27	dioxolane	84	PhCO <sub>2</sub> <sup>-</sup>	$2.3 \times 10^{-6}$	240	30	4.6
28	dioxolane	9	Cl <sup>-</sup>	$3.5 \times 10^{-7}$	3600	77	11
29	dioxolane	39	Cl <sup>-</sup>	$3.5 \times 10^{-7}$	3600	23	14
30	dioxolane	104	Cl <sup>-</sup>	$3.5 \times 10^{-7}$	3600	9	15
31	benzodiox <sup>f</sup>	40	Cl <sup>-</sup>	$3.5 \times 10^{-7}$	3600	2	1.8
32	dioxolane	38	Cl <sup>-</sup>	$2.3 \times 10^{-6}$	600	58	1.6
33	THF	40	Cl <sup>-</sup>	$2.3 \times 10^{-6}$	600	65	1.9
34 <sup>e</sup>	dioxolane	42	Cl <sup>-</sup>	$2.3 \times 10^{-6}$	600	62	1.9
35 <sup>e</sup>	THF	43	Cl <sup>-</sup>	$2.3 \times 10^{-6}$	600	56	1.7
36 <sup>e</sup>	dioxolane	41	Cl <sup>-</sup>	$2.3 \times 10^{-6}$	300	43	2.6
37 <sup>e</sup>	dioxolane	41	Cl <sup>-</sup>	$1.1 \times 10^{-6}$ <sup>g</sup>	300	27	3.4
38 <sup>e</sup>	dioxolane	41	Cl <sup>-</sup>	$2.0 \times 10^{-6}$ <sup>g</sup>	300	28	19
39 <sup>e</sup>	dioxolane	43	Cl <sup>-</sup>	$1.5 \times 10^{-6}$	120-600 <sup>h</sup>	4-25 <sup>h</sup>	8.7
40 <sup>e</sup>	THF	34	Cl <sup>-</sup>	$2.3 \times 10^{-6}$	120-600 <sup>h</sup>	18-90 <sup>h</sup>	2.0

<sup>a</sup> All photolyses were carried out at room temperature using rigorously degassed reaction solutions unless otherwise noted. <sup>b</sup> Determined using the benzophenone-benzhydrol actinometer. <sup>c</sup> Percent yield based on [1] as determined by GC. <sup>d</sup> Quantum yield for formation of ArI. <sup>e</sup> Undegassed reaction solutions. <sup>f</sup> 1,3-Benzodioxole. <sup>g</sup> Calculated from absorbance of light attenuators placed between the light source and reaction tube. <sup>h</sup> Reaction followed as a function of irradiation time. See Figure 1 (expt 40). Five points were obtained in the specified intervals.

Rüchardt and co-workers<sup>24</sup> have reported that both THF and dioxolane also reduce arenediazonium salts in a chain process completely analogous to the propagation steps, eqs 4-6, for reduction of iodonium salt. We found that reduction of *p*-toluenediazonium hexafluorophosphate (0.06 M) by THF (3.8 M) in acetone-*d*<sub>6</sub> solution, with initiation by visible light (200-W floodlamp) photolysis of PAIBN (0.03 M),<sup>25</sup> gives a reaction that is zero order in diazonium concentration (Figure 2). In addition, the product ratio of toluene (TolH) to benzene (the product of initiation by phenyl radicals from PAIBN) remains constant over at least the last four points in Figure 2 at [TolH]/[PhH] = 13 ± 1. Since this ratio reflects the chain length of the THF/diazonium reaction,<sup>26</sup> iodonium and diazonium salts are reduced by THF with equal chain lengths. The proposal outlined in the preceding paragraph is, thus, demonstrated; zero-order kinetics and an invariant chain length equal to the rate ratio of  $\alpha$ - to  $\beta$ -hydrogen abstraction are expected for THF reduction of any arylonium salt (as long as  $\alpha$ -THF<sup>•</sup> transfers an electron to the onium ion with  $k \geq 10^6$  M<sup>-1</sup> s<sup>-1</sup>).

The quantum yield of photolysis of iodonium salt in THF is not expected to depend on light intensity and should equal about 2 ( $k_\alpha/k_\beta \times \Phi_i$ ) regardless of photolysis conditions (see previous discussion). The agreement

(22) We have not measured  $k_\alpha/k_\beta$  directly and we know of no such measurement reported in the literature. However, Minisci and co-workers<sup>23a</sup> obtained an 85% yield of the  $\alpha$ -substituted THF product in the aryl-radical-mediated reaction of 4-cyanopyridine with THF. This places a lower limit on  $k_\alpha/k_\beta$  of 85:15 (5.7). In comparison, the hydroxyl radical has been reported to react with THF with  $k_\alpha/k_\beta = 92:8$  (11.5).<sup>23b</sup> Also see refs 23c,d.

(23) (a) Minisci, F.; Vismara, E.; Fontana, F.; Morini, G.; Serravalle, M. *J. Org. Chem.* 1986, 51, 4411-4416. (b) Eibenberger, J.; Schulte-Frohlinde, D.; Steenken, S. *J. Phys. Chem.* 1980, 84, 704-710. (c) Malatesta, V.; Ingold, K. U. *J. Am. Chem. Soc.* 1981, 103, 609-614. (d) Malatesta, V.; Scaliano, J. C. *J. Org. Chem.* 1982, 47, 1455-1459.

(24) (a) Rüchardt, C.; Merz, E.; Freudenberg, B.; Oppenorth, H.-J.; Tan, C.-C.; Werner, R. *Essays on Free-Radical Chemistry*; Special Publication 24; The Chemical Society: London, 1970; pp 51-70. (b) Werner, R.; Rüchardt, C. *Tetrahedron Lett.* 1969, 2407-2412.

(25) This concentration was high enough to ensure that the rate of initiation was constant (i.e.,  $A(395 \text{ nm}) = 2.0$  at 50% consumption of the initiator).

(26) Irradiation of an otherwise identical diazonium solution which omitted PAIBN gave <2% toluene after 7.5 min, demonstrating that other initiation processes are not available.

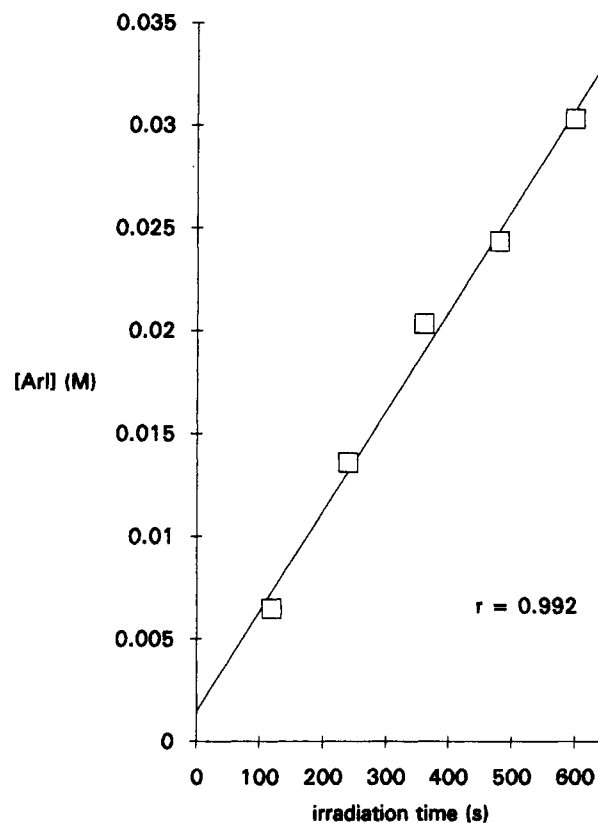


Figure 1. Photolysis at 313 nm of diaryliodonium salt 1 in THF.

between our results (expts 33, 35, and 40, Table 2), a previously reported result ( $\Phi_{\text{THF}} = 2$ ),<sup>27</sup> and the predicted value is excellent. However, dioxolane is in general the more reactive ether, in agreement with the observed order of reactivity of these ethers with diazonium salts.<sup>24</sup> This is primarily a consequence of the fact that  $\approx 10\%$  of all aryl radicals in THF always lead to termination by reaction at the  $\beta$ -position. In contrast, no unproductive mode of reaction of aryl radicals with dioxolane exists because both

(27) Gatechair, L. R. Ph.D. Thesis, North Dakota State University, 1980, p 31. Also see ref 10d, p 22.

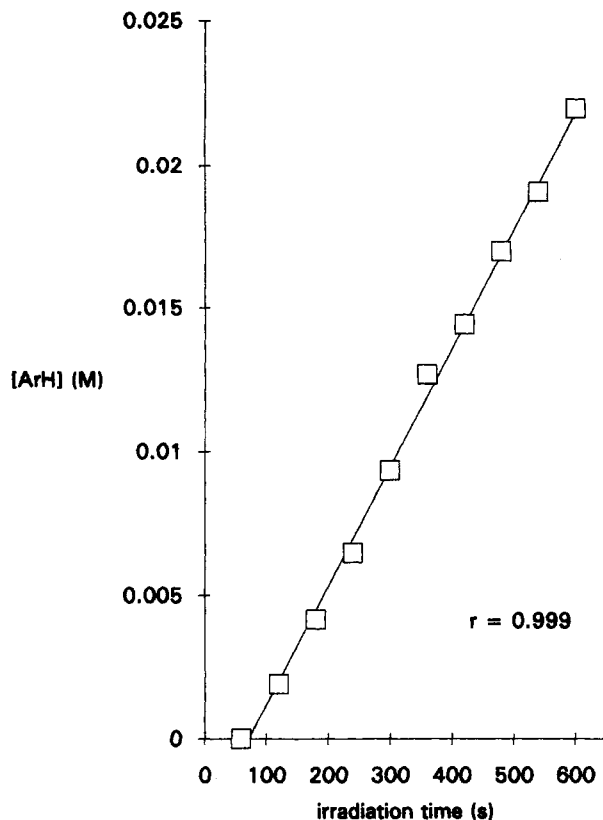


Figure 2. PAIBN-initiated reduction of *p*-toluenediazonium hexafluorophosphate in THF solution.

Table 3. Thermodynamics of SET from Ether-Derived Radicals to Onium Salts

radical	$E(\text{ox})^a$ V vs SCE	$\Delta G^\circ(\text{SET})$ , kcal/mol		
		$\text{ArN}_2^+{}^b$	$\text{Ar}_2\text{I}^+{}^c$	$\text{Ar}_3\text{S}^+{}^d$
$\alpha$ -THF <sup>e</sup>	-0.35	-13.8	+8.1	+19.6
2-dioxolanyl	-0.85 <sup>e</sup>	-25.3	-3.5	+8.1
4-dioxolanyl	-0.35 <sup>f</sup>	-13.8	+8.1	+19.6
dioxanyl	-0.08	-7.6	+14.3	+25.8
phosphoranyl	+1.68 <sup>g</sup>	-44.4	-13.9	-10.7

<sup>a</sup> Reference 28a except where otherwise noted. <sup>b</sup>  $E_{1/2}(\text{red}) = +0.250$  V vs SCE for Ar = *p*-tolyl. Reference 29. <sup>c</sup>  $E_{1/2}(\text{red}) = -0.7$  V vs SCE. Reference 3b. An earlier value ( $E_{1/2}(\text{red}) = -0.2$  V vs Ag/AgCl, reference 30) assigned to the reduction of adsorbed iodonium at the electrode surface has often been used. See refs 10d and 31. <sup>d</sup>  $E_{1/2}(\text{red}) = -1.2$  V vs SCE. Reference 32. <sup>e</sup> Reference 28b. <sup>f</sup> Assumed equal to  $\alpha$ -THF<sup>e</sup>. <sup>g</sup>  $E_{1/2}(\text{red}) = -1.68$  V vs SCE for tetraarylophosphonium salts. Reference 33.

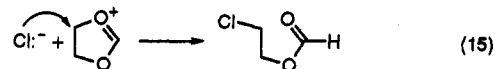
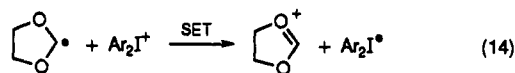
the 2-dioxolanyl and 4-dioxolanyl radicals have sufficient reducing power to transfer an electron to the iodonium salt<sup>28</sup> (Table 3).<sup>29–32</sup> Since reaction of aryl radical is ca. 2.5 times faster at the 4-position of 1,3-dioxolane<sup>33</sup> the 4-dioxolanyl radical must be the primary chain carrier in the reductions by dioxolane.

Two experiments using different ethers are worthy of comment. The PAIBN-initiated reaction of iodonium salt 1 was slower in 1,4-dioxane than in either dioxolane or THF (expts 19–21, Table 2). 1,4-Dioxane presents only

one site for reaction with aryl radical; the slower relative rate is simply a consequence of the poorer reducing ability of the 2-dioxanyl radical vs  $\alpha$ -THF<sup>e</sup> and the dioxolanyl radicals<sup>28</sup> (Table 3). The other experiment allows a comparison of the rates of photolysis of 1 in dioxolane vs 1,3-benzodioxole (expts 29 and 31, Table 2). The latter ether gave an approximately 10-fold slower reaction as expected from the fact that addition of phenyl radicals to the benzene ring (a termination step) must compete strongly with the relatively slow hydrogen abstraction from the acetal carbon (see later discussion).<sup>34,35,36</sup>

$\beta$ -Chloroethyl formate ( $\text{HCO}_2\text{CH}_2\text{CH}_2\text{Cl}$ ) was detected as a minor product in dioxolane solutions that gave high yields of reduced products, ArI and ArH (expts 1, 3, 4, 7, 8, and 10, Table 1). This product corresponds to trapping of some of the oxonium ions formed by the transfer of an electron from the 2-dioxolanyl radical to the iodonium salt (eqs 14 and 15).<sup>37</sup> The  $\beta$ -chloro ester might be formed directly (eq 15) or by way of 2-chlorodioxolane as an intermediate.<sup>38</sup> In either case, the oxidation state of this solvent-derived ester clearly demonstrates the role of solvent as a reductant. The formation of this product also shows that chloride terminates polymerization by trapping the propagating oxonium ion center. On the other hand the basic underlying iodonium chemistry is unaffected by the presence of halide ion.

Reaction of diaryliodonium hexafluorophosphate salts in ethers under the same nonphotochemical conditions that give a clean redox radical-chain reaction of iodonium chloride 1 led to rapid polymerization of the ether solvent (Table 4, expts 41, 43, and 46). Control reactions that



omitted either the radical initiator (expts 42, 44, and 47) or the iodonium salt (expts 45 and 48) gave no polymerization (except when the reaction flask was not shielded from incidental room light in expt 42). These results clearly tie the radical-chain chemistry of 1 to the polymerization chemistry of iodonium salts with nonnucleophilic counteranions. In other words, a radical chain reduction

(34) A rate constant for addition of phenyl radical to benzene ( $k_{\text{add}} = 4.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) has been reported.<sup>16</sup> In comparison, hydrogen abstraction from the acetal position of 1,3-dioxolane is ca. 5 times slower than abstraction of  $\alpha$ -hydrogens from THF (see footnote 35). This allows a rate constant of ca.  $1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  to be estimated for acetal hydrogen abstractions (see footnote 15).

(35) From a literature value<sup>36a</sup> for the relative rate of reaction of phenyl with THF vs with dioxolane,  $k_{\text{THF}}/k_{\text{dioxolane}} = 0.92$ , and assuming that  $k_a/k_p \approx 10$  for THF and that the 4-hydrogens of dioxolane have equal reactivity to the  $\alpha$ -hydrogens of THF, a value of  $k_4/k_2 \approx 2.5$  (per H) can be deduced. This is in line with the suggestion by Růchardt and co-workers<sup>36b</sup> that anomeric stabilization of the reactant by a second alkoxy substituent should retard hydrogen abstractions from acetal positions.

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(37) Since the ester is also a product of the thermally-initiated dark reactions (expts 1 and 10, Table 1) it is not a photochemical product. In addition, iodonium benzoate photolyzes at essentially the same rate as the chloride (expts 24 and 26, Table 2), ruling out any mechanism for formation of the ester which involves chloride in a rate-determining process.

(38) Cort, L. A.; Pearson, R. G. *J. Chem. Soc.* 1959, 1682–1687.

(28) (a) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* 1988, 110, 132–137. (b) Wayner, D. D. M. Personal communication.

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(31) (a) Pappas, S. P.; Jilek, J. H. *Photogr. Sci. Eng.* 1979, 23, 140–143.

(b) Galli, C. *Chem. Rev.* 1988, 88, 765–792.

(32) McKinney, P. S.; Rosenthal, S. *J. Electroanal. Chem. Interfacial Electrochem.* 1968, 16, 261–270.

(33) Horner, L.; Röttger, F.; Fuchs, H. *Chem. Ber.* 1963, 96, 3141–3147.

**Table 4. Polymerization of Ether Solutions of Diaryliodonium Hexafluorophosphates ((*p*-R-Ph)<sub>2</sub>I<sup>+</sup>PF<sub>6</sub><sup>-</sup>) and Thermal Radical Initiators**

expt	R	concn, <sup>a</sup> M	solvent	init <sup>b</sup>	[init], M	conds <sup>c</sup>	gel time, h
41	CH <sub>3</sub>	0.10	dioxolane	AIBN	0.012	75 °C	0.5
42	CH <sub>3</sub>	0.10	dioxolane	none		75 °C	20
43	<i>t</i> -Bu	0.02	dioxolane	DBPO	0.002	rt, dark	<8 <sup>d</sup>
44	<i>t</i> -Bu	0.02	dioxolane	none		rt, dark	>142 <sup>e</sup>
45	none	0.02	dioxolane	DBPO	0.003	rt, dark	>144 <sup>e</sup>
46	<i>t</i> -Bu	0.02	THF	DBPO	0.003	rt, dark	<15 <sup>d</sup>
47	<i>t</i> -Bu	0.03	THF	none		rt, dark	>125 <sup>e</sup>
48	none	0.03	THF	DBPO	0.004	rt, dark	>120 <sup>e</sup>

<sup>a</sup> Initial concentration of iodonium salt. <sup>b</sup> Radical initiator used. AIBN = azobisisobutyronitrile. DBPO = di-*tert*-butyl peroxalate. <sup>c</sup> Dark reactions were shielded from incidental room light by aluminum foil. <sup>d</sup> The reaction solution had set up to a hard, clear solid polymer within the time indicated. <sup>e</sup> Gelation was not observed in the time indicated.

**Table 5. Polymerization of THF by Visible Light Irradiation<sup>a</sup> of Onium Salt-TMP-THF Solutions**

expt	onium salt <sup>b</sup> (concn, mM)	[TMP], M	[PAIBN], mM	time, h	% convn <sup>c</sup>
49 <sup>d</sup>	Ar <sub>2</sub> I <sup>+</sup> (30)	none	15	6.0	11 <sup>e</sup>
50	Ar <sub>2</sub> I <sup>+</sup> (13)	0.23	none	3.7 24 <sup>f</sup>	30 <sup>f</sup> 76
51	Ar <sub>2</sub> I <sup>+</sup> (21)	none	none	1.5	0
52 <sup>h</sup>	Ar <sub>2</sub> I <sup>+</sup> (21)	<i>h</i>	none	1.0	0 <sup>i</sup>
53	ArS <sup>+</sup> Ph <sub>2</sub> (2.4)	0.14	6	6.0	2.6 <sup>j</sup>
54	ArS <sup>+</sup> Ph <sub>2</sub> (2.4)	0.18	none	6.0	0 <sup>j</sup>
55	ArS <sup>+</sup> Ph <sub>2</sub> (2.4)	none	5	6.0	0 <sup>j</sup>

<sup>a</sup> A 200-W floodlamp was used. <sup>b</sup> The hexafluorophosphate salts were used. Ar = *p*-methylphenyl. <sup>c</sup> Percent conversion of THF to poly-THF by <sup>1</sup>H NMR. <sup>d</sup> THF-*d*<sub>8</sub> was used. <sup>e</sup> Conversion of Ar<sub>2</sub>I<sup>+</sup> to (relative yields in parentheses) ArI (53%), ArH (47%), was 69%. <sup>f</sup> Conversion of Ar<sub>2</sub>I<sup>+</sup> to (relative yields in parentheses) ArI (50%), ArH (25%), and ArPO(OMe)<sub>2</sub> (25%) was 100%. <sup>g</sup> Dark period after initial photolysis. <sup>h</sup> Triphenylphosphine (0.1 M) was an additional reactant. <sup>i</sup> Conversion of Ar<sub>2</sub>I<sup>+</sup> to (relative yields in parentheses) ArI (50%), ArH (33%), and ArP<sup>+</sup>Ph<sub>3</sub> (17%) was ≈100%. <sup>j</sup> Analysis performed 72 h after termination of photolysis.

of iodonium salt gives monomer-derived oxonium ions that start cationic polymerizations (eqs 5–8).

In fact, the chemistry of iodonium salts with nonnucleophilic anions can be directly observed in the polymerizing systems. When a solution of di-*p*-tolylidonium hexafluorophosphate (0.03 M) and PAIBN (0.015 M) in THF-*d*<sub>8</sub> was irradiated with a 200-W incandescent bulb, 69% conversion (by <sup>1</sup>H NMR) of iodonium salt to *p*-deuterio-toluene (TolD) and *p*-iodotoluene (TolI) occurred in 6 h (expt 49, Table V). Conversion of residual protio-THF to poly-THF at this point was only 11% (by NMR). However, the reaction mixture set up to a solid polymer within a few days. In another experiment, a 0.03 M THF-*d*<sub>8</sub> solution of the ditolyliodonium salt was irradiated at 313 nm for 33 min, resulting in 60% conversion of iodonium salt to TolD and TolI and ca. 15% conversion of protio-THF to poly-THF (expt 50, Table 5). This reaction solution solidified within an hour following the irradiation period. Evidently, the "living" polymerization<sup>10,11</sup> of THF-*d*<sub>8</sub> is slow enough under these conditions to allow observation of the radical-chain reaction that starts it.

According to two previous reports,<sup>39,40</sup> triarylsulfonium salts do not initiate cationic polymerization in the presence

of radical sources. Our experiments show that the redox chain between THF and triarylsulfonium ion also fails. Accordingly, when a solution of *p*-tolylidiphenylsulfonium hexafluorophosphate (0.06 M) and PAIBN (0.024 M) in THF-*d*<sub>8</sub> was irradiated with a 200-W incandescent bulb, no reaction was observable (by <sup>1</sup>H NMR) after 30 h. The polymerization fails because the redox chain to give oxonium ion fails. As Crivello has pointed out,<sup>10d</sup> the difference in behavior between sulfonium and iodonium salts is due to the fact that sulfonium salt is a poorer oxidizing agent (Table 3). In fact, the free energy of electron transfer from α-THF<sup>•</sup> to sulfonium is unfavorable by ca. 20 kcal/mol. Therefore, it is not surprising that chain propagation by electron transfer to onium salt fails in this case.

Triarylsulfonium salts, despite their nonreactivity in the radical chain process, nevertheless do function as efficient UV photoinitiators of cationic polymerization.<sup>41</sup> This means that processes other than the radical-chain mechanism, which is the focus of this paper, must be able to give polymerization initiating species. By analogy, it is reasonable that this should also be the case with the iodonium-initiated polymerizations. The proton mechanism in the form originally proposed by Crivello for both iodonium (eqs 1–4) and sulfonium polymerization systems is unlikely<sup>42</sup> because the hydrogen abstractions (eq 2) by the heteroatom radical cations, Ar<sub>2</sub>S<sup>•+</sup> and ArI<sup>•+</sup>, from the ethers involve breaking a strong carbon–hydrogen bond with the concomitant formation of an extraordinarily weak bond.<sup>43</sup> On the other hand, Hacker and Dektar<sup>3a,45</sup> and Saeva<sup>46</sup> have done a good job of clarifying the pathways by which the radical cations do produce protons in acetonitrile solution. Undoubtedly, both a radical-cation/proton pathway and the redox radical-chain mechanism operate in the photoinitiation of cationic polymerizations by iodonium salts. However, since only the radical chain can give multiple polymerization starting cations per photon absorbed, it must be viewed as the primary mechanism of the iodonium-photoinitiated polymerizations.

The results reported in this paper establish that radical-chain reduction of onium salts by electron-donor radicals can give oxonium ions that can start cationic polymerization. The reduction of iodonium by ether-derived radicals, however, is a relatively slow, short chain. Furthermore, these radicals do not reduce sulfonium salts.

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(41) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Lett. Ed.* 1979, 17, 759–764.

(42) This has been pointed out previously. See ref 32a.

(43) This is especially true for the iodonium system. A dissociation energy of 10–30 kcal/mol for the iodoarene–hydrogen bond, [ArI]<sup>•+</sup>–H, can be estimated using a thermodynamic cycle and literature values of ionization potentials, IP(PhI) = 8.7 eV<sup>44a</sup> and IP(H) = 13.595 eV,<sup>44b</sup> and the proton affinity of iodobenzene, PA(PhI) = 5.4–6.1 eV.<sup>44c</sup> This means that eq 2 is endoergic by at least 60 kcal/mol! The hydrogen abstraction by the sulfinyl radical cation (eq 18) is more reasonable because of the greater basicity of sulfide, PA(R<sub>2</sub>S) = 9.15 eV<sup>44d</sup> (IP(PhSMe) = 7.93 eV<sup>44a</sup> gives a dissociation energy of ca. 80 kcal/mol for the diaryl sulfide–hydrogen bond, [Ar<sub>2</sub>S]<sup>•+</sup>–H).

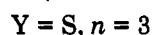
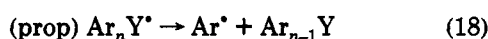
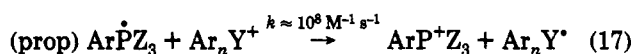
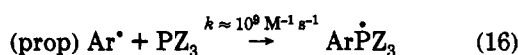
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Clearly, a more effective electron-donor radical could give a higher quantum yield for formation of initiating cations in the iodonium system and might even be oxidized by sulfonium ions. We have recently reported<sup>9d</sup> that arylphosphoranyl radicals ( $\text{Ar}\dot{\text{P}}\text{Z}_3$ ) are effective reductants for both iodonium and sulfonium salts. In addition, aryl radicals add rapidly to trivalent phosphorus. Accordingly, the reduction of diaryliodonium and triarylsulfonium hexafluorophosphates by certain phosphines ( $\text{PZ}_3$ ) proceeds with long chain lengths to give arylphosphonium salts ( $\text{ArP}^+\text{Z}_3$ ) (eqs 16–18). The phosphine chains are better than the ether chains both because phosphine reacts with phenyl radicals (eq 16) without unproductive competing reactions (i.e.,  $\beta$ -hydrogen abstraction from THF) and because phosphoranyl is a better reductant<sup>33</sup> than the ether-derived radicals (see Table 3).



When  $\text{Z} = \text{OMe}$ , the reaction of trimethyl phosphite (TMP) with onium salt can be photoinitiated with visible light to give an aryltrimethoxyphosphonium salt which, because of its methylating ability, can start cationic polymerizations (eqs 19 and 20). Accordingly, visible light irradiation of a THF solution of di-*p*-tolyliodonium hexafluorophosphate and trimethyl phosphite results in polymerization of the solvent (expt 50, Table 5). The iodonium salt is converted to *p*-iodotoluene, toluene, and dimethyl *p*-tolylphosphonate ( $\text{TolPO}(\text{OMe})_2$ ), the last product a result of the trimethoxyphosphonium salt acting as a methylating agent (eq 19). Omission of the trimethyl phosphite gives a much slower polymerization (expts 49 and 51, Table 5) and substitution of triphenylphosphine for TMP (expt 52, Table 5) gives no polymer despite ca. 100% conversion of iodonium to *p*-iodotoluene, toluene, and *p*-tolyltriphenylphosphonium salt. These results clearly demonstrate the special role of TMP as a reductant that gives a phosphonium salt capable of starting polymerization.



The dramatic rate enhancement by TMP comes about even though only half of the intermediate aryl radicals react with the TMP (as indicated by the equal yields of arene and aryl phosphonate in expt 50, Table 5). If the THF-derived radicals that result from the competing hydrogen abstraction by aryl radicals could react only by the same pathways as are available in the absence of TMP, then the rate enhancement could not be so dramatic.<sup>47</sup> Therefore, we conclude that the  $\beta$ -THF radicals, which terminate in the absence of phosphite, are scavenged by TMP to give phosphoranyl radical intermediates that propagate a long chain by rapidly transferring an electron to the iodonium salt.

The use of TMP as a means to harness cationic polymerizations to radical-chain reductions of onium salts should also work for sulfonium salts<sup>9d</sup> and represents a novel method for photopolymerization by sulfonium salts. However, the photolysis of triarylsulfonium salts by visible light is inefficient<sup>9e</sup> and another means of photoinitiation is required. Irradiation for 6 h with a 200-W floodlamp of a THF solution of *p*-tolylidiphenylsulfonium hexafluorophosphate, TMP, and PAIBN gave 2.6% conversion of THF to poly-THF (expt 53, Table 5). Omission of either TMP or PAIBN gave no polymer (expts 54 and 55, Table 5). These results, while not optimized, demonstrate that the principle of the proposed sulfonium/TMP photoinitiation system is correct. Further work is obviously necessary. In principle, the onium/TMP polymerization systems should not require monomers capable of chain reduction of onium salt. If these ideas are correct, a new class of monomers not photopolymerizable by onium salts and visible light may be photopolymerized by onium/TMP mixtures.<sup>48</sup>

Finally, we note that many of the reactions reported in this paper have been initiated by photolysis in the visible region of the spectrum. In some cases, a charge-transfer complex of iodonium and phosphine may be responsible for the long-wavelength absorption.<sup>9b</sup> More generally, the use of PAIBN ( $\lambda_{\text{max}} = 395 \text{ nm}$ ) as a free-radical initiator for the redox chains represents a new approach to cationic polymerizations with long wavelength light.<sup>49</sup>

In conclusion, radical-chain reduction of iodonium salts by cyclic ethers (eqs 5–7) gives ether-derived oxonium ions that can either be captured by nucleophilic counteranions (e.g., eq 15) or start cationic polymerization of the ether (eq 8). In certain cases a limitation on the chain length of these reactions is imposed by the nonselectivity of aryl radicals in hydrogen abstraction reactions from the ethers (e.g., eq 12). In addition, the redox characteristics of the ether-derived radicals are important. Finally, radical-chain reduction of both iodonium and sulfonium salts by trimethyl phosphite gives intermediate aryltrimethoxyphosphonium salts (eqs 16–18) that can also initiate cationic polymerization of THF (eqs 19 and 20).

## Experimental Section

<sup>1</sup>H NMR spectra were recorded at 400 MHz. Spectral data are reported in ppm and are normalized to residual proton resonances of the respective solvent ( $\beta$ -protio-THF-*d*<sub>7</sub>,  $\delta$  1.73;  $\text{CHCl}_3$ ,  $\delta$  7.24,  $\text{CD}_3\text{COCD}_2\text{H}$ ,  $\delta$  2.04). Mass spectra were recorded at 70 eV. IR spectra were recorded on a grating spectrophotometer. Analytical GC was carried out using thermal conductivity detectors with helium as the carrier gas. The column used was 10-ft  $\times$  1/8-in. 10% FFAP on Chromosorb P AW, 60/80 mesh. Peaks were integrated digitally by a personal computer and/or by triangulation and peak identities confirmed either through

(47) Steady-state treatment leads to the conclusion that the kinetic chain length for formation of polymerization-starting cations would be improved by an amount equal to the rate ratio of aryl radical capture by TMP to nonproductive  $\beta$ -hydrogen abstraction from THF. At this [TMP] this rate ratio is ca. 10:1 (calculated from the product ratio  $[\text{ArP}(\text{O})(\text{OMe})_2]:[\text{ArH}]$  and our estimate that  $\beta$ -hydrogen abstraction is 10 times slower than  $\alpha$ -hydrogen abstraction). Therefore, the chain length without TMP (previously shown to be about 10) would only be improved by a factor of 2.

(48) TMP can presumably also act as a chain-transfer agent in cationic polymerizations. Therefore, the average molecular weight of the polymer may be lowered in the TMP/onium systems.

(49) Other approaches have included the use of various photosensitizers, modification of the structure of the onium salt in order to either extend its absorption into the visible or make it more easily reduced, and the use of visible light sensitive radical sources in the iodonium system.<sup>10d</sup>

collection (4-ft  $\times$  1/4-in. 10% FFAP on Chromosorb P AW column) and  $^1\text{H}$  NMR or MS analysis or by coinjection with authentic materials. Naphthalene was used as an internal standard and peak areas were corrected using response factors generated from mixtures of pure compounds.

Benzene, THF, 1,3-dioxolane, and 1,4-dioxane were distilled from sodium/benzophenone under  $\text{N}_2$  immediately before use. (Dioxolane was pretreated according to a standard procedure.<sup>50</sup>) 1,3-Benzodioxole was distilled from sodium under  $\text{N}_2$ . Benzophenone and benzhydrol were recrystallized from petroleum ether. *tert*-Butylbenzene, azobis(isobutyronitrile) (AIBN), and naphthalene were obtained from commercial sources and not purified. 4,4'-Di-*tert*-butyldiphenyliodonium chloride (1) and hexafluorophosphate salts,<sup>10</sup>  $\beta$ -chloroethyl formate,<sup>38</sup> 4-*tert*-butylchlorobenzene,<sup>51</sup> and 4-*tert*-butylnitrobenzene<sup>52</sup> were prepared by literature procedures. All other compounds used in this study were described previously.<sup>9d</sup>

**4,4'-Di-*tert*-butyldiphenyliodonium Benzoate.** This salt was prepared from the chloride (5.5 g, 13 mmol) by anion metathesis using 3.2 g (14 mmol)  $\text{Ag}_2\text{O}$ <sup>10a,b</sup> and 20 mL of 0.6 M sodium benzoate in methanol. The crude product was collected (4.3 g, 65%) and recrystallized from acetone to give pure white crystals (2.7 g, 41%): mp 174–175 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.27 (s, 18 H), 7.3 (overlapping triplets, 3 H), 7.4 (d, 4 H,  $J = 8$  Hz), 7.8 (d, 4 H,  $J = 8$  Hz), 8.0 (d, 2 H,  $J = 6$  Hz); IR (KBr) 2960, 1590, 1535, 1370  $\text{cm}^{-1}$ ; MS  $m/z$  393 ( $\text{M}^+$ ), 260.

**4-*tert*-Butyliodobenzene.** Reduction of 4-*tert*-butylnitrobenzene with  $\text{Fe}/\text{HCl}$  to give 4-*tert*-butylaniline, followed by diazotization and KI treatment, gave ca. 90% pure 4-*tert*-butyliodobenzene after distillation: yield 47%, bp 118–120 °C (4 Torr). The iodo compound was purified to >99% GC purity by preparative GC.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.27 (s, 9 H), 7.12 (d, 2 H,  $J = 8.6$  Hz), 7.57 (d, 2 H,  $J = 8.5$  Hz). IR (neat) 2960, 1495, 1390, 1000, 820, 715  $\text{cm}^{-1}$ . MS:  $m/z$  260 ( $\text{M}^+$ ), 245, 118.

**General Experimental Procedures.** A Hanovia SH Model medium-pressure Hg arc in conjunction with a 0.002 M  $\text{K}_2\text{CrO}_4$  in 1%  $\text{K}_2\text{CO}_3$ (aq) filter solution was used for irradiation at 313 nm (expts 22–40).<sup>53</sup> Broad-band UV irradiation was carried out with the Hg arc, filtering out lower frequencies using a 20-mm-thick Plexiglas slab (expts 3–6).<sup>54</sup> Irradiation with visible light was carried out with a 200-W industrial floodlamp either at a distance of 2–3 cm from the tube containing the reaction solution (expts 50–53) (cooling provided by a vigorous stream of room temperature air) or directing the light beam through a 10-cm photochemical cell containing 10% (w/w)  $\text{NaNO}_2$ (aq) as a filter solution (expts 15–18).<sup>55</sup> Additionally,<sup>56</sup> a 275-W sunlamp (expts 7 and 8) and the Hg arc with a 4.5 M  $\text{NaNO}_2$ (aq) filter solution (expts 19–21) were used for some of the experiments. Dark experiments were carried out in reaction vessels which were tightly wrapped with aluminum foil.

Dry Pyrex reaction vessels were used and care was taken to keep the reaction solutions anhydrous. Reactions were either followed to completion by TLC and GC analyzed after addition of internal standard or filtered through alumina to remove unreacted iodonium salt after internal standard addition before GC analysis.

**Quantum Yield Determination.**<sup>13</sup> Benzene solutions of benzophenone ( $\text{Ph}_2\text{CO}$ ; 0.94 M) and benzhydrol ( $\text{Ph}_2\text{CHOH}$ ; 28, 56, 113, 169, 225, 338, 451 mM) were prepared in pairs in 1.5-cm Pyrex tubes and degassed by three freeze–pump–thaw cycles to 0.001 Torr. One of each of the pairs of tubes was then photolyzed simultaneously with the others at 313 nm for 90 min. The light source was housed in a quartz photochemical immersion well

and reaction vessel filled with the 313-nm filter solution and was allowed to warm up for 30 min before the photolysis. A Pyrex absorption sleeve was used in order to reduce the light intensity. After photolysis 1.0-mL aliquots were withdrawn and diluted 1:25 with benzene. The unphotolyzed tubes were treated identically. Conversion of benzophenone in the actinometer solutions was deduced from the ratio of absorbances at 330, 335, 340, 345, and 350 nm of the irradiated to the nonirradiated solutions, averaging the results obtained over the five wavelengths.

The results were treated both by using eq 21<sup>57</sup> with a least-squares treatment of  $\Phi_{\text{act}}/\Phi_{\text{sam}}$  vs  $[\text{Ph}_2\text{CHOH}]^{-1}$ , giving  $\Phi_{\text{act}}$  and

$$I_0 = \frac{\% \text{ convn (act)}}{100} \times [\text{Ph}_2\text{CO}] \times \Phi_{\text{act}}^{-1} \quad (21)$$

$I_0$  and by using eq 22<sup>13</sup> individually for each of the solutions and averaging the results to obtain the intensity,  $I_0$ . The average result using the first method was  $(1.34 \pm 0.02) \times 10^{-6}$  einstein  $\text{s}^{-1} \text{L}^{-1}$ .<sup>58</sup> (Correlation coefficients were greater than 0.97.) The other method gave  $I_0 = 1.6 \pm 0.1 \times 10^{-6}$  einstein  $\text{s}^{-1} \text{L}^{-1}$ . The average of results obtained by the two methods,  $I_0 = 1.5 \times 10^{-6}$  einstein  $\text{s}^{-1} \text{L}^{-1}$ , was used.

$$I_0 = \frac{0.033 \ln \frac{100}{100 - \% \text{ conv}} + [\text{Ph}_2\text{CO}]_0 - [\text{Ph}_2\text{CO}]_t}{t} \quad (22)$$

Simultaneous photolysis of three tubes (expt 22) containing a 0.047 M dioxolane solution of iodonium salt 1 for 5.0 min gave an average GC yield of 4-*tert*-butyliodobenzene of  $6.4 \pm 0.4$  mM. This result combined with the result for  $I_0$  gives the quantum yield reported.

The other quantum yields reported in Table 2 are less reliable and make use of intensity measurements made for different light source housings (all quartz housing,  $I_0 = 2.3 \times 10^{-6}$  einstein  $\text{s}^{-1} \text{L}^{-1}$ ; all Pyrex housing,  $I_0 = 3.5 \times 10^{-7}$  einstein  $\text{s}^{-1} \text{L}^{-1}$ ) not necessarily carried out simultaneously with the iodonium photolyses. Experiments 37 and 38 made use of intensity attenuators (wire gauze,  $A(313) = 0.28$ ; and weighing paper,  $A(313) = 1.04$ ) placed between reaction tubes and the light source.

**Kinetics Experiment.** A stock solution of 1 in THF (0.033 M, expt 40, Figure 1) was partitioned in 5-mL portions between five dry  $15 \times 1.5$  cm Pyrex test tubes. The tubes were placed on a merry-go-round apparatus all at the same time (after allowing the lamp to warm up ca. 30 min) and then pulled off at regular 2.0-min intervals.

**NMR Experiments (Expts 49–56 and Figure 2).** Experiments carried out in THF- $d_6$  (expts 49 and 50) or THF/ $\text{CD}_3\text{-COCD}_3$  (Figure 2) were run in NMR tubes and directly analyzed by  $^1\text{H}$  NMR. Reactions using THF as solvent were run on a larger scale with aliquots removed and diluted in  $\text{CDCl}_3$  for NMR analysis. Conversions and relative yields were deduced from the integral of the resonance of the *p*-Me protons of the starting onium salt ( $\text{ToI}_2\text{I}^+$ ,  $\delta$  2.37;  $\text{ToI}^+\text{Ph}_2$ ,  $\delta$  2.51;  $\text{ToI}^+\text{N}_2^+$ ,  $\delta$  2.61) and of key resonances of the products (*p*-Me protons:  $\text{ToI}$ ,  $\delta$  2.26;  $\text{ToIH}$ ,  $\delta$  2.31;  $\text{ToIPO}(\text{OMe})_2$ , 2.40;  $\text{ToIP}^+\text{Ph}_3$ , 2.52. Ring protons:  $\text{PhH}$ ,  $\delta$  7.30). Conversion of THF to poly-THF was calculated from the ratio of the integrals of resonances at  $\delta$  3.32 and 1.52 (assigned to poly-THF, literature values are  $\delta$  3.4, 1.63)<sup>56</sup> to the integrals of the THF peaks ( $\delta$  3.58, 1.73).

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