VALIDITY OF RATE FACTORS IN FREE RADICAL AROMATIC SUBSTITUTION[1]

Sir:

The validity of rate factors derived from data on isomer distribution and substrate competition in free radical aromatic substitution,[2,3] and of theoretical discussions based on them, has been seriously questioned[4,5,6] chiefly, and properly, on the basis of certain isotope effects[4] and the finding of products formed by dimerization (4)[7] and disproportionation (5)[5] of arylcyclohexadienyl radicals, ArAr'H·. Eliel, *et al.*,[4] found no selectivity in consumption of deuterated and ordinary substrates but a significant product isotope effect, attributed to preferential hydrogen abstraction in (3), (5), and (6), with resulting diversion of ArAr'D· to dimer (4) and, perhaps, of $ArAr'D_2$ and ArAr'DH to polymer. Isolation of biaryl in the absence of oxygen, which otherwise participates in (6), increases the effect several-fold, indicating the importance of the (5), (6) sequence. Here, clearly, product composition is not a true measure of the relative rates at which Ar'H and Ar'D undergo (2). It was suggested that, in a similar way, isomer distribution (and, presumably, competition data) may not be a true measure of the relative rates of formation of *o*-ArAr'H·, *m*-ArAr'H·, and *p*-ArAr'H· (or ArAr'H· and ArAr''H·).

$$(\mathrm{ArCOO})_2 \longrightarrow 2\mathrm{ArCOO}\cdot \longrightarrow \mathrm{Ar}\cdot + \mathrm{CO_2} \tag{1}$$

$$\mathrm{Ar}\cdot + \mathrm{Ar'H} \longrightarrow \mathrm{ArAr'H}\cdot \tag{2}$$

$$\mathrm{ArAr'H}\cdot + \text{oxid. agent} \longrightarrow \mathrm{ArAr'} \tag{3}$$

$$2\mathrm{ArAr'H}\cdot \longrightarrow (\mathrm{ArAr'H})_2 \tag{4}$$

$$2\mathrm{ArAr'H}\cdot \longrightarrow \mathrm{ArAr'H_2} + \mathrm{ArAr'} \tag{5}$$

$$\mathrm{ArAr'H_2} + \text{oxid. agent} \longrightarrow \mathrm{ArAr'} \tag{6}$$

Recently, Eberhardt and Eliel[8] have found that the presence of oxygen during aroyl peroxide decomposition in benzene dramatically increases the yield of biaryl, evidently by speeding up (3) and perhaps (6) at the expense of (4), (5), and other side-reactions, and point out that isomer distribution determined under these conditions should be a truer measure of rate factors than are previous data.

Using gas chromatographic analysis, we have studied phenylation by benzoyl peroxide of four substituted benzenes in both the absence and the presence of oxygen. Substituent groups include the *o,p*-directing nitro, the strongly *o*-directing methoxyl, and the bulky *t*-butyl. Table I shows that, even though biaryl yields are increased as much as three-fold by oxygen, isomer distribution and relative reactivities remain unchanged. If side-reactions following (2) are selective and reduce the yields of isomeric biaryls or of differently substituted biaryls to different extents, then suppressing the side-reactions to a fraction of their former importance must result in a change in distribution or relative reactivity. The results force one to conclude that, however unlikely it might have seemed *a priori*, such side-reactions are non-selective.

TABLE I

ARYLATION[a] OF C_6H_5X IN PRESENCE AND ABSENCE OF OXYGEN

			Biaryls produced[c]				
		Substrate		Isomer distribution, %			
X	O_2[b]	ratio[d]	Yield[d]	*o*	*m*	*p*	*f*[e]
CH_3O	−	60	0.50	69.8	14.7	15.6	1.99[f]
	+	60	0.73	69.7	14.5	15.7	..
	+	600	1.08	69.6	14.5	16.0	..
	+	600[g]	1.35	69.8	14.5	15.8	2.01
Br	−	60	0.33	56.2	27.3	16.5	1.14[f]
	+	600	0.95	55.8	27.8	16.5	..
	+	600[g]	1.58	55.2	28.8	16.0	1.11
NO_2	−	600	0.17	62.8	9.5	27.7	..
	+	600	.61	63.1	10.1	26.9	..
	−	600[g]	.19	63.2	9.7	27.1	2.95
	+	600[g]	.68	62.8	9.7	27.5	2.85
t-C_4H_9	−	600[g]	(.72)	(21.2)	(49.9)	(29.0)	(0.63)
	+	600[g]	(1.40)	(21.2)	(50.0)	(28.8)	(0.61)

[a] Unless otherwise specified, with benzoyl peroxide at 80°. [b] Bubbled through solution at about 15–20 cc. per min. [c] Values in parentheses have not been corrected for relative thermal responses, but are quite suitable for comparison. [d] Moles per mole arylating agent. [e] Total rate factor, measured against benzene. [f] From a separate competition run. [g] Equimolar mixture of C_6H_5X and benzene.

Actually, for years such non-selectivity has been strongly indicated by a large body of evidence: for a particular substrate-radical combination, isomer distribution and relative reactivity are essentially unaffected by wide variations in reaction conditions[2]—temperature,[9,10] nature[10,11] or (within limits) concentration[11,12,13] of arylating agent, presence of other substrates[12,13,14]—which often causes changes[9,10,13] (by factors as large as seven[9]) in biaryl yield. The special significance of the present work is that the way in which oxygen affects the yield is understood—at least to the same extent as the evidence[4,5,7] that has raised this whole question—and pretty clearly involves suppression of side-reactions *following*[15] initial attack (2). Consideration shows[16] that the changes in

---

[1] This work was supported by a research grant from the Air Force Office of Scientific Research and the National Science Foundation Research Participation Program.

[2] D. R. Augood and G. H. Williams, *Chem. Revs.*, **57**, 123 (1957).

[3] G. H. Williams, "International Series of Monographs on Organic Chemistry, Volume 4, Homolytic Aromatic Substitution," Pergamon Press, Inc., New York, N. Y., 1960.

[4] E. L. Eliel, S. Meyerson, Z. Welvart and S. H. Wilen, *J. Am. Chem. Soc.*, **82**, 2936 (1960).

[5] D. F. DeTar and R. A. J. Long, *ibid.*, **80**, 4742 (1958); D. F. DeTar Abstracts 17th National Organic Chemistry Symposium Am. Chem. Soc., Bloomington, Ind., 1961, pp. 64–70.

[6] D. F. DeTar, *J. Am. Chem. Soc.*, **83**, 1014 (1961).

[7] (a) B. M. Lynch and K. H. Pausacker, *Austral. J. Chem.*, **10**, 40 (1957); (b) K. H. Pausacker, *ibid.*, **10**, 49 (1957); B. M. Lynch and K. H. Pausacker, *ibid.*, **10**, 165 (1957).

[8] M. Eberhardt and E. L. Eliel, *J. Org. Chem.*, **27**, 2289 (1962).

[9] L. K. Dyall and K. H. Pausacker, *J. Chem. Soc.*, 18 (1961).

[10] D. F. DeTar and H. J. Schiefele, *J. Am. Chem. Soc.*, **73**, 1442 (1951); D. H. Hey, C. J. M. Stirling and G. H. Williams, *J. Chem. Soc.*, 2747 (1954).

[11] C. S. Rondestvedt and H. S. Blanchard, *J. Am. Chem. Soc.*, **77**, 1769 (1955).

[12] D. Bosniack, Ph.D. Thesis, New York University, 1961.

[13] A. Cain, Ph.D. Thesis, New York University, 1962.

[14] O. C. Dermer and M. T. Edmison, *Chem. Revs.*, **57**, 77 (1957).

[15] Although side-reactions *competing with* (2), such as attack by aroyloxy radicals on a side-chain or to produce ester, have often been cited (ref. 7a and 17) as invalidating competition data, this does not seem a valid point, so long as the arylation that *does* occur involves an aryl radical that is free to "choose" between substrate molecules. Low biaryl yields *per se* have no bearing on validity.

[16] This is discussed in detail in ref. 12.

[17] C. S. Rondestvedt and H. S. Blanchard, *J. Org. Chem.*, **21**, 229 (1956); D. I. Davies, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 3112 (1961); B. M. Lynch and R. B. Moore, *Canad. J. Chem.*, **40**, 1461 (1962); and others.

yield caused by other variations in experimental conditions must also, partly at least, involve the competition of (3) *versus* (4) and (5). Isotope effects indicate that, as would be expected, the (5), (6) sequence "is a more important path at low benzoyl peroxide concentration than at high. . . ."[4] The presence of benzene as a competing substrate adds a ArAr''H· species to undergo cross-combination (4) and cross-disproportionation (5) with the original *o*-, *m*-, and *p*-ArAr'H·; yet, as illustrated in Table I, isomer distribution is unchanged, showing that in their interactions the various arylcyclohexadienyl radicals are converted randomly into biaryls or side-products. The same randomness is indicated by the constancy of relative reactivity, which requires that oxygen (to pick one experimental variable) increase the yield of biphenyl by exactly the same factor as the yield of substituted biphenyl, and yet by a factor that is different for each substrate mixture.

There is no inconsistency between the isotope effects[4] and the present findings. Whereas the ease of abstraction of hydrogen should certainly be affected by its atomic weight, consideration shows[16] that it is not at all unreasonable that ease of abstraction from the reactive species ArAr'H· should be little affected by the nature or position of a substituent, or by steric factors. In any case, however it is explained, the evidence shows clearly that side-reactions have no significant effect on isomer distribution and relative reactivities measured by product analysis, and that such data provide valid rate factors for free radical aromatic substitution.

(18) Department of Chemistry, Clarkson College of Technology, Potsdam, N. Y.

DEPARTMENT OF CHEMISTRY
NEW YORK UNIVERSITY
WASHINGTON SQUARE
NEW YORK, N. Y.

ROBERT T. MORRISON
JACK CAZES
NORMAN SAMKOFF
CHARLES A. HOWE[18]

RECEIVED AUGUST 16, 1962

SPONTANEOUS FORMATION OF RADICAL-ANIONS FROM NITROAROMATICS IN BASIC SOLUTION[1,2]

Sir:

p- and *o*-nitrotoluene spontaneously form radical-anions in the presence of potassium *t*-butoxide in *t*-butyl alcohol or dimethyl sulfoxide. A 0.0025 *M* solution of *p*-nitrotoluene in the presence of 0.06 *M* potassium *t*-butoxide in *t*-butyl alcohol under nitrogen gave a product containing about 0.0016 *M* unpaired spins (by comparison of e.s.r. absorption with that of diphenylpicrylhydrazyl) after 1 hr. at 30°. The e.s.r. spectrum obtained in dimethyl sulfoxide–*t*-butyl alcohol (4:1) containing excess potassium *t*-butoxide reproduces in all detail the seventy line spectrum reported for the *p*-nitrotoluene radical-anion in acetonitrile.[3] In *t*-butyl alcohol a forty line spectrum is observed (Fig. 1) which is consistent with a radical-anion with $a_{\mathrm{N}} = 12.7$, $a_{\alpha\text{-H}} \sim a_{o\text{-H}} = 3.4 \pm 0.1$, $a_{m\text{-H}} = 1.1 \pm 0.1$ gauss.[4]

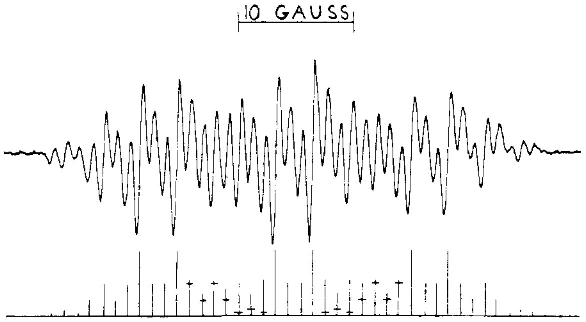

Fig. 1.—Radical-anion formed from reaction of potassium *t*-butoxide with *p*-nitrotoluene in *t*-butyl alcohol solution. Spectrum obtained with a Varian V-5400 EPR spectrometer using 100 kc. field modulation. Synthetic spectrum composed from hyperfine splitting constants given in text.

In *t*-butyl alcohol appreciable amounts of radicals are formed by the interaction of potassium *t*-butoxide with *p*-nitroethylbenzene, *o*-nitroethylbenzene, *o*-bromo-*p*-nitrotoluene, *p*-nitro-*o*-xylene, *o*-amino-*p*-nitrotoluene, *p*-nitrobenzyl alcohol, *p*-nitrobenzaldehyde, 2-nitrofluorene, *p*-nitroacenaphthalene and *m*-dinitrobenzene. Under these conditions all of the above compounds, as well as *o*- and *p*-nitrotoluene, react readily with oxygen to form a variety of products.[5] In the presence of excess *t*-butoxide ion no radicals, or only traces of radicals, were detected from *m*-nitrotoluene, nitrobenzene, 1,3,5-trinitrobenzene, 2,4,6-trinitrotoluene, tris-(*p*-nitrophenyl)-methane, *p*-nitrocumene, 2,2',4,4'-tetranitrodiphenylmethane, phenylnitromethane, α-nitroacetophenone, 2-nitropropane, 2-nitro-1,3-indandione and *p*-nitrophenylacetonitrile. For these compounds little, if any, reaction with oxygen was observed and it seems safe to conclude that generally, *aromatic nitro compounds which oxidize readily in basic solution spontaneously form free radicals in the absence of oxygen.*

2,4-Dinitrotoluene spontaneously forms only a low concentration of radical-ions in the presence of excess base but forms significant amounts of radical-anions in deficient base. This result suggests that radical-anion formation often involves electron transfer between the ionized and unionized nitrocompound.[6]

If solutions of *p*-nitrotoluene (0.1 *M*) in *t*-butyl alcohol are acidified with excess water and then treated with oxygen, nearly all the starting material can be accounted for in recovered *p*-nitrotoluene and *p,p'*-dinitrobibenzyl, provided the reaction time is short. After periods longer than those in Table I, the products become complex with the formation of polymeric substances containing azo or azoxy linkages.[7]

(1) Reactions of Resonance Stabilized Anions. III.

(2) Grateful acknowledgment is made of support of this work by grants from the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society.

(3) A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852 (1961).

(4) These constants differ from those reported in acetonitrile solution.[3] Solvent effects on hyperfine splitting constants have been observed previously (E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **36**, 1944 (1962)); L. H. Piette, P. Ludwig and R. N. Adams, *ibid.*, **83**, 3904 (1961); Y. Deguchi, *Bull. Chem. Soc. Japan*, **35**, 260 (1962).

(5) Anthony J. Moye, Ph.D. Thesis, Iowa State University, 1961.

(6) In this connection it is pertinent to point out that the nitroalkanes (G. A. Russell, *J. Am. Chem. Soc.*, **76**, 1595 (1954)) as well as tris-(*p*-nitrophenyl)-methane react more readily with oxygen in the presence of deficient potassium *t*-butoxide in *t*-butyl alcohol than in the presence of excess base.

(7) For example, see A. G. Green, *J. Chem. Soc.*, **85**, 1424 (1904).