

Kinetics of Hydrogen Isotope Exchange Reactions. Part XXII.¹ Reactivity Comparisons for a Series of Aromatic Substrates towards Radiolytically Generated Tritium Atoms in Aqueous Solution

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The relative reactivities of a series of aromatic compounds towards tritium atoms, generated by β -radiolysis, have been determined in degassed aqueous solution by a competition method, involving copper(II) ions as common competitor in the radiation-induced aromatic hydrogen exchange. Under these conditions, steps subsequent to the formation of the cyclohexadienyl radical are not kinetically significant. It is shown that comparable doses of γ -irradiation induce an equivalent extent of exchange. From the effect of low concentrations of copper(II) ions on the β -radiation-induced exchange rate it is concluded that the reversion of the intermediate cyclohexadienyl radical to aromatic compound normally involves an oxidation step [reaction with residual oxygen or copper(II)], and that bimolecular radical-radical reactions are unimportant. The rates of tritium atom attack relative to benzene are: mesitylene, 8.5; toluene, 2.2; anisole, 2.7; fluorobenzene, 1.0; chlorobenzene, 1.1; bromobenzene, 1.1; benzonitrile, 0.9; trifluoromethylbenzene, 0.35; and t-butylbenzene, ca. 2–4. Because of an intramolecular kinetic isotope effect, the rate of radiation-induced tritium uptake by mesitylene is ca. 1.5 ± 0.2 times larger than that by [2,4,6-²H₃]mesitylene. The extinction coefficients at the u.v. absorption maxima for these substrates in aqueous solution have been redetermined. The solubility of t-butylbenzene in water at 25° was found to be $(1.9 \pm 0.1) \times 10^{-2}$ g dm⁻³. The rate constant for the reaction of hydrogen (tritium) atoms with iodide ion is ca. 5.5×10^7 dm³ s⁻¹ mol⁻¹.

THE reaction of tritium atoms, produced by the self-radiolysis of tritiated water, with dissolved mesitylene² and benzene³ has previously been shown to lead to tritium labelling of the aromatic solute. From the effect of copper(II) ion, a well-recognised competitor for hydrogen (tritium) atoms, on the rate of exchange for the two substrates it was found that mesitylene is ca. 8 times more reactive than benzene towards tritium atoms.³ The same conclusion was reached by a direct competition experiment between benzene and mesitylene.³

The present work extends our earlier investigations^{2,3} in three main respects. First, the new data relate to experiments on de-gassed solutions, whereas partially aerated solutions were used before. This is relevant because of the known reactivity of oxygen towards some of the products of the radiation chemistry of water.⁴ Secondly, it is now shown that brief periods of γ -irradiation, resulting in a comparable radiation dose to that achieved by the self-radiolysis from tritium decay in the solution, bring about comparable amounts of aromatic hydrogen exchange. These experiments constitute a crucial test of our basic interpretation of these exchange reactions as radiation-induced processes. The third and chief objective of the present work is the measurement of substituent effects on the rate of the radiation-induced exchange for a range of aromatic compounds. This allows the conclusion about the relative reactivity of these compounds towards hydrogen (tritium) atoms, which was previously based on the single comparison of mesitylene with benzene, to be somewhat more generalised. Most of the data given are the first reported measurements of the reactivity of the re-

spective compounds towards hydrogen atoms in aqueous solution. Since our method relies on a different technique and chemical reaction as a probe for this purpose, the reactivity pattern obtained is complementary to other approaches to this problem.⁵⁻⁷ A preliminary account of the present work has been published.⁸

EXPERIMENTAL

Except as noted in the following, the materials and general methods employed were the same as in preceding work.^{2,3}

Aromatic compounds other than mesitylene were purified by successive washings with AnalaR concentrated sulphuric acid (five times) and water (five times), drying (molecular sieve, 4 Å). This was followed by preparative-scale g.l.c. (F and M 770–775, with a range of stationary phases). Hydrochloric acid was the AristaR product. All other inorganic reagents were of AnalaR quality.

[2,4,6-²H₃]Mesitylene was prepared by shaking mesitylene (2 cm³) for 30 min with [²H₂]sulphuric acid (3 cm³) (prepared from sulphur trioxide and D₂O) to form the sulphonic acid, followed by addition of deuterium oxide (3 cm³), standing (7 days) and heating to convert the sulphonic acid back to mesitylene. After isolation of the product the entire procedure was repeated and the product gas-chromatographed twice on a 5 m Carbowax column at 165°. Protium content in aromatic positions was less than 5% (by n.m.r.).

Procedure for Radiation-induced Exchange Measurements. Reactions were carried out in 30 cm³ ampoules closed by ungreased Rotaflo TF/18 Teflon stopcocks and fitted with standard cones for attachment to a vacuum line. Glassware (reaction vessels and syringes, with the exception of the gas-tight Hamilton syringe reserved for transfers of tritiated water) was cleaned by overnight immersion in a 1:1 (v/v) mixture of fuming nitric acid and sulphuric

¹ Part XXI, V. Gold, J. R. Lee, and A. Gitter, *J. Chem. Soc. (B)*, 1971, 32.

² J. R. Adsetts and V. Gold, *Chem. Comm.*, 1968, 915; *J. Chem. Soc. (B)*, 1969, 1108.

³ J. R. Adsetts and V. Gold, *Chem. Comm.*, 1969, 353; *J. Chem. Soc. (B)*, 1969, 1114.

⁴ M. Anbar and P. Neta, *J. Appl. Radiation Isotopes*, 1967, 18, 493.

⁵ M. Anbar, D. Meyerstein, and P. Neta, *Nature*, 1966, 209, 1348.

⁶ M. C. Sauer, jun., and I. Mani, *J. Phys. Chem.*, 1970, 74, 59.

⁷ P. Neta and R. H. Schuler, *J. Amer. Chem. Soc.*, 1972, 94, 1056.

⁸ C. L. Brett and V. Gold, *Chem. Comm.*, 1971, 148.

acid at 100°, followed by continuous-flow washing in water for several hours, rinsing successively in distilled and triple-distilled water and drying (at 400° for reaction vessels, 120° for volumetric ware). Teflon stopcocks were washed in an ultrasonic bath and dried at 60°. Reaction mixtures were made up in the ampoules by syringe transfers, in order, of the following solutions, all at 25°: scavenger stock solution (if any), water (to bring the volume at that stage to 10 cm³), stock solution of aromatic substrate (14.0 cm³ in most experiments, by Cheney adaptor to ensure reproducibility), and tritiated water (1 cm³ from Hamilton syringe with Cheney adaptor). Ampoules were then attached to the vacuum line, and the samples (generally in batches of four) de-gassed by three cycles of freezing (liquid air), pumping (0.002 mmHg, measured on a Pirani gauge), and melting. (Breakage of Pyrex ampoules due to thermal expansion of frozen solutions is avoided by sudden immersion of the liquid-air cooled tube in boiling water.) A similar procedure is reported⁹ to lead to a final oxygen concentration of ca. 10⁻⁶M.

After a suitable reaction period (normally 5 days), in a thermostatted bath at 25° for self-irradiation, the tubes were opened by removal of the Teflon stopcock key. The sample from each ampoule was withdrawn through a Teflon needle into a 30 cm³ syringe and discharged into a test tube containing a weighed amount of the aromatic compound as carrier (normally 2 cm³) together with 2 cm³ of n-hexane, the tip of the needle being below the surface of the organic layer. Reaction vessel and syringe were rinsed once with water and the washings added into the test tube. The test tube was then closed with a ground-glass stopper and shaken mechanically (30 min) for complete equilibration and extraction of labelled solute into the carrier phase. The lower layer of tritiated water was removed and the organic layer washed with distilled water by a continuous-flow method, the water being added from above the organic phase and withdrawn through the centre tube of a Drechsel head from below the organic layer after percolating through it. The procedure is an improvement on the repeated batch extraction method formerly used,^{2,3} and permitted complete removal of tritiated water from a batch of four samples within ca. 1.25 h. After being dried (molecular sieve, 4 Å) for at least 3 days, the samples were subjected to g.l.c. and the aromatic component was collected and counted.

Except where stated otherwise, the tabulated results refer to β-radiolysis and a temperature of 25°. Self-radiolysis from β-decay was considered to start after the second stage of de-gassing and to finish on shaking with carrier after admission of air.

Concentration Measurement.—The stock solutions of aromatic compounds used for making up reaction mixtures were generally nearly saturated, and the concentration was determined either by spectrophotometry or (in the case of t-butylbenzene only) by analytical g.l.c. The required extinction coefficients of the aromatic compounds in aqueous solution were obtained (Table I) by measurements (Unicam SP 500) either on solutions prepared from a stock solution in ethanol by double dilution with water (method A) or on solutions made up by direct injection from a Hamilton syringe of precise amounts (1–10 μl) into

water (100 cm³) and shaking for 30 min (method B). In the case of benzene both methods were used, as well as a modification of method B ('method C') in which the water is contained in the barrel of a larger syringe and the injection of aromatic compound from the Hamilton syringe is made through the tip of the larger syringe which is then capped and dissolution achieved by magnetic stirring.

TABLE I

U.v. absorption maxima and extinction coefficients of aromatic substances in aqueous solution

Compound	$\lambda_{\max.}/\text{nm}$	$\epsilon_{\max.}/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ^a	Solution method
Anisole	269.5	1425 ± 25 (1479, ^b 1585 ^c)	B
Benzene	253.0	150 ± 5 (500, ^d 300, ^e 150 ^f)	A, B, C
Benzonitrile	270.0	950 ± 20 (1000 ^{g,h})	B
Bromobenzene	260.5	158 ± 5 (191 ^b)	A
Chlorobenzene	263.5	176 ± 5 (191 ^b)	A
Fluorobenzene	259.5	610 ± 15 (513 ^b)	B
Mesitylene	263.5	217 ± 5 (-)	A
Toluene	261.5	236 ± 5 (229 ^c)	A

^a Literature values are given in parentheses. ^b J. W. Bridges and R. T. Williams, *Nature*, 1962, **196**, 59. ^c W. F. Forbes, A. S. Ralph, and R. Gosine, *Canad. J. Chem.*, 1959, **37**, 1305; cf. J. C. Dearden and W. F. Forbes, *ibid.*, 1958, **36**, 869. ^d M. A. Kenonkh and E. M. Lapinskaya, *Doklady Akad. Nauk, S.S.S.R.*, 1965, 125. ^e J. M. Vandenberg, *Appl. Spectroscopy*, 1963, **17**, 120 (methanol solution). ^f R. L. Bohon and W. F. Claussen, *J. Amer. Chem. Soc.*, 1951, **73**, 1571 (ethanol solution). ^g With 2% methanol.

The solubility of t-butylbenzene was too low for these procedures to be convenient. Saturated stock solutions were used and their concentration established by injection of 5 μl samples of aqueous solution into an analytical gas chromatograph (Varian 1200). The response of the instrument to t-butylbenzene was established by use of standard solutions of t-butylbenzene in n-hexane under the same operating conditions. The concentration of a saturated solution of t-butylbenzene in water at 25° was found to be (1.4 ± 0.1) × 10⁻⁴M, or (1.9 ± 0.1) × 10⁻² g dm⁻³.

Trifluoromethylbenzene solutions were made up by volume (10 μl Hamilton syringe).

γ-Irradiation Procedure and Dosimetry.—The cobalt-60 source (ca. 9 kCi) at Imperial College was used in these experiments.* The usual sample ampoules were placed in the same position, ca. 20 cm from the centre, and the radiation dose received at that position was established with the Fricke dosimeter ([FeSO₄] = 0.0014M, [NaCl] = 0.001M, [H₂SO₄] = 0.4M). An extinction coefficient at 305 nm of 2195 dm³ mol⁻¹ cm⁻¹ and a G value of 15.5 Fe³⁺ ions per 100 eV (16 aJ) were used in the calculation of dose rates,¹¹ which were of the order of 8000 rad min⁻¹ (1.355 J kg⁻¹ s⁻¹). The temperature of the irradiation chamber was ca. 22°.

Radioactivity Assay.—The general procedure and equipment were described by Gold and Rolston,^{10,12} except that a paper-tape punch attachment to the counter was used to record results. Averaging, background subtraction, and quench correction by the external standards ratio

* Rolston and Gold¹⁰ erroneously gave the intensity of the source as 1.7 kCi.

¹¹ J. J. Weiss, A. O. Allen, and H. A. Schwarz, *Proc. Int. Conf. Peaceful Uses Atomic Energy*, United Nations, New York, 1956, **14**, 179; E. J. Fendler and J. H. Fendler, *Progr. Phys. Org. Chem.*, 1970, **7**, 229.

¹² V. Gold and J. H. Rolston, *J. Chem. Soc. (B)*, 1970, 1795.

⁹ E. J. Hart and E. M. Fielden, *Adv. in Chem. Series*, 1965, **50**, 253.

¹⁰ J. H. Rolston and V. Gold, *J. Chem. Soc. (B)*, 1970, 1808.

method were performed by the University of London-King's College CDC 6600/1700 computer system.

Specimen Calculation.—Exchange rates were calculated from measured activities as the activity (disintegrations min^{-1} , d.p.m.) acquired by the solute contained in one litre of reaction solution per day (units: d.p.m. $\text{day}^{-1} \text{dm}^{-3}$, where 1 d.p.m. $\text{day}^{-1} \text{dm}^{-3} = 1.929 \times 10^{-7} \text{s}^{-2} \text{dm}^{-3} = 5.21 \text{aCi s}^{-1} \text{dm}^{-3}$).

In a typical experiment 25 cm^3 of a solution of anisole ($2.743 \times 10^{-3} \text{M}$) containing 7.312 Ci dm^{-3} of tritiated water, after self-irradiation for 5.108 days, was extracted with anisole-hexane containing 1.954 g of anisole as carrier. After purification, 0.9041 g of anisole were counted giving 1041.7 ± 5.2 counts min^{-1} (c.p.m.). The background was 26.9 c.p.m. and the counting efficiency 0.485, which gives the total activity of anisole in 1 l of solution as $[(1041.7 - 26.9)/0.485] \times (5.108)^{-1} \times (1.954/0.9041) \times 40 = 35420$ d.p.m. $\text{day}^{-1} \text{dm}^{-3}$.

In comparisons, these rates were generally corrected to the same activity of tritium in the solution (1 Ci dm^{-3}) by dividing by the square of the activity, on the assumption that measured exchange rates are proportional to the square of the tritium concentration (see below). On this basis, the result becomes $35,420/(7.312)^2 = 662$ d.p.m. $\text{day}^{-1} \text{dm}^3 \text{Ci}^{-2}$ (where 1 d.p.m. $\text{day}^{-1} \text{dm}^3 \text{Ci}^{-2} = 1.409 \times 10^{-31} \text{s}^{-4} \text{m}^3$).

Kinetic Measurements on Hydrogen Exchange in Mesitylene during β -Radiolysis.—It was established that essentially no exchange occurred during de-gassing and work-up; that the rate of tritium uptake in de-gassed samples was approximately three times that in partially aerated solution; and that for de-gassed solutions the amount of exchange was proportional to reaction time. Most measurements on this compound were performed with [1,3,5- ^{14}C]-mesitylene, the ^{14}C activity of extracts with carrier mesitylene being used to correct the tritium activities of the extracts for radiation damage of the sample (Table 2). The dependence of exchange rate on mesitylene concentra-

TABLE 2

Comparison of exchange rates for degassed and partially aerated solutions of mesitylene

Tritium activity of water = 6.94 Ci dm^{-3} ; [mesitylene] = $1.92 \times 10^{-4} \text{M}$

Reaction time/day	Carbon-14 activity/ c.p.m. dm^{-3}	Corrected * tritium activity/ c.p.m. dm^{-3}	Exchange rate/ c.p.m. $\text{day}^{-1} \text{dm}^3 \text{Ci}^{-2}$	Sample type
0	281	0		De-gassed
3.9	248	703	180	Partially aerated
3.9	253	2796	717	De-gassed
8.0	206	1783	223	Partially aerated
8.0	201	5850	731	De-gassed

* Corrected activity = observed activity \times (^{14}C activity of zero-time sample/ ^{14}C activity of sample).

tion (Table 3) and on tritium concentration (Table 4) establishes that a limiting exchange rate is reached at low concentrations of mesitylene for de-gassed solutions and that the amount of exchange at these concentrations is proportional to the square of the tritium concentration (Table 5). The dependence of exchange rate on concentration of aromatic substance was also established for

TABLE 3

Variation of the exchange rate with concentration of [^{14}C]mesitylene

Tritium activity of water = 6.94 Ci dm^{-3} ; reaction time = 6 days

10^4 [Mesitylene]/M	Carbon-14 (calc.)/c.p.m.	Carbon-14 (obs.)/c.p.m.	Exchange rate/ d.p.m. $\text{day}^{-1} \text{dm}^3 \text{Ci}^{-2}$ ^a
0.63	103	66	474
1.26	205	167	544
1.88	307	265	562
2.51	410	371	552
3.14	512	451	533
3.77	615	557	593
5.02	820	770	594
(5.23)	854 ^b)

^a These figures are observed rates corrected for damage via a formula analogous to that given in Table 2. The values in column 2 represent the calculated ^{14}C activity for a zero-time sample. ^b This is the total ^{14}C content of 25 cm^3 of the stock solution of mesitylene.

TABLE 4

Variation of exchange rate with concentration of [2,4,6- ^3H]₃mesitylene (A)

Tritium activity of water = 6.43 Ci dm^{-3} ; reaction time = 5 days

10^4 [(A)]/M	Exchange rate/ d.p.m. $\text{day}^{-1} \text{dm}^3 \text{Ci}^{-2}$
0.00	0.0
0.19	232
0.38	319
0.76	392
1.14	397
1.90	480
2.66	502
3.62	505
4.57	531

TABLE 5

Dependence of mesitylene exchange rate on tritium concentration

[Mesitylene] = $4.53 \times 10^{-4} \text{M}$; reaction time = 5 days

Tritium activity of water/ Ci dm^{-3}	Carbon-14/ c.p.m.	Exchange rate/ d.p.m. $\text{day}^{-1} (25 \text{cm}^3)^{-1}$ ^a	Corrected exchange rate/ d.p.m. $\text{day}^{-1} \text{dm}^3 \text{Ci}^{-2}$ ^b
(0.00 ^c)	550)
6.43	546	605	584
12.86	495	2808	680
19.30	507	5863	624
25.73	457	10,744	648

^a Exchange rates corrected for radiation damage as in Table 2. ^b Value in column 3 divided by square of tritium activity. ^c Zero time sample for carbon-14 assay.

TABLE 6

Variation of exchange rate with chlorobenzene concentration

Tritium activity of water = 6.43 Ci dm^{-3} ; reaction time = 5 days

10^3 [Chlorobenzene]/M	Exchange rate/ d.p.m. $\text{day}^{-1} \text{dm}^3 \text{Ci}^{-2}$ ^a
0.00	0
0.36	349
0.72	384
1.08	424
1.44	415
1.80	418
2.16	453
2.88	425

^a Radiation damage to this substrate is considered negligible; no correction for damage was made.

[2,4,6-²H₃]mesitylene (Table 4) and chlorobenzene for the latter of these the limiting rate appears to be reached at a concentration of *ca.* 10⁻³M (Table 6).

Tests for Formation of Cyclohexadienes in β-Radiolysis of Benzene Solutions (Experiments by E. LEONIDOU).—Solutions of benzene (5.3 × 10⁻³M) in tritiated water were allowed to exchange according to the procedure described above. After six days each sample was added to a mixture of benzene, cyclohexa-1,3-diene, and cyclohexa-1,4-diene (1 ml of each), shaken for *ca.* 30 min and, after the layers had been allowed to settle, subjected to the usual continuous-flow washing and drying. Each sample was then further diluted with a mixture of 2 ml of each of the three carrier hydrocarbons and subjected to g.l.c. on a column previously shown to allow clean separation of the components (2,2-dihydroxypropionitrile, 35% on firebrick, 4 m column at 80°). An aliquot portion of each fraction was assayed for tritium. The activity of benzene in the three samples corresponded to 281 and 312 d.p.m. (per day per sample) for experiments in the presence of 9.3 × 10⁻³M-copper sulphate, and 496 d.p.m. for an experiment in the absence of added scavengers. No activity was detectable above background in any of the cyclohexadiene fractions. The formation of these compounds cannot therefore account for more than *ca.* 1% of the activity of the benzene samples in the main sets of experiments for which the gas-chromatographic separation technique used did not separate the substrate from possible cyclohexadiene by-products.

Use of Re-distilled Tritiated Water.—Some exchange measurements on toluene were conducted both with unpurified tritiated water and with a sample purified by refluxing (3 h) and distillation from alkaline permanganate in a closed-circuit still similar to that described by Coatsworth *et al.*¹³ One of the solutions for the experiment with unpurified tritiated water contained an equal volume of triple-distilled water after redistillation from the same still. No significant differences were found.

Effect of Added Gases.—Admission of nitrogen to the reaction vessel after de-gassing appears to have no effect on the exchange rate, whereas oxygen (1 atm) reduces the rate to less than one-tenth. These findings are in line with the observed difference between de-gassed and partially aerated solutions (Table 2) and establish that oxygen is, as expected, the responsible component of air.

Competition Studies.—Two types of competition experiment were performed. The first involved the effect of added solutes on the increase in activity of the aromatic substrate, without examination of the product of the scavenger reaction (see Tables 7–12). The second employed two aromatic solutes in competition in the same solution, and the exchange rates of both substances were examined (see Tables 13–15). The objectives of these experiments were the development of a satisfactory kinetic model for the reactions occurring and the systematic measurement of relative reactivities for a series of aromatic compounds.

In the direct competition experiments between two solutes the carrier consisted of approximately equal volumes (usually 2 cm³) of each compound. The carrier extracts were washed, dried, and separated by temperature-programmed preparative g.l.c.

Results of γ-Radiolysis.—Measurements on [1,3,5-¹⁴C]-mesitylene established the dependence of the exchange

rate on dose (Table 16), concentration of aromatic solute (Table 17), and concentration of added copper(II) sulphate (Table 18).

TABLE 7
Competition experiments with copper(II) sulphate
(Reaction time = 5 days)

Substrate	10 ³ [Substrate]/M	Tritium activity of water/ Ci dm ⁻³	10 ³ [CuSO ₄]/M	Exchange rate/ d.p.m. day ⁻¹ dm ³ Ci ⁻¹	
Benzene	4.72	7.32	0	595	
	4.72	7.32	25	422	
	4.72	7.32	50	398	
	4.72	7.32	75	355	
	4.72	7.32	100	346	
	4.72	7.32	200	260	
	4.72	7.32	350	203	
	4.72	7.32	500	153	
Toluene	1.10	7.31	0	557	
	1.10	7.31	25	324	
	1.10	7.31	50	269	
	1.10	7.31	75	230	
	1.10	7.31	100	227	
	1.10	7.31	200	161	
	1.10	7.31	350	112	
	1.10	7.31	500	89	
Mesitylene ^a	0.265	6.94	0	503	
	0.265	6.94	102	173	
	0.265	6.94	205	118	
	0.265	6.94	307	97	
	0.279	6.94	0	503	
	0.279	6.94	40	246	
	0.279	6.94	81	185	
	0.279	6.94	121	160	
	0.279	6.94	202	122	
	0.279	6.94	302	98	
	[³ H ₃]Mesitylene	0.265	7.75	0	458
		0.265	7.75	25	241
0.265		7.75	50	215	
0.265		7.75	100	176	
0.265		7.75	200	112	
0.265		7.75	300	82	
0.265		7.75	400	76	
0.265		7.75	500	92 ²	
Anisole		2.74	7.31	0	662
		2.74	7.31	25	539
	2.74	7.31	50	488	
	2.74	7.31	75	441	
	2.74	7.31	200	348	
	2.74	7.31	350	268	
	2.74	7.31	500	219	
Fluorobenzene	3.32	7.32	0	743	
	3.32	7.32	50	324	
	3.32	7.32	100	261	
	3.32	7.32	200	196	
	3.32	7.32	300	159	
	3.32	7.32	400	134	
	3.32	7.32	500	114	
Chlorobenzene	1.13	7.32	0	350, 350	
	1.13	7.32	50	176	
	1.13	7.32	200	84	
	1.13	7.32	300	67	
	1.13	7.32	400	55	
Bromobenzene	1.72	7.75	0	435	
	1.72	7.75	25	274	
	1.72	7.75	50	232	
	1.72	7.75	75	199	
	1.72	7.75	100	187	
	1.72	7.75	200	141	
	1.72	7.75	350	91	
	1.72	7.75	500	71	
Benzonitrile	2.13	7.31	0	480	
	2.13	7.31	25	344	
	2.13	7.31	50	301	
	2.13	7.31	75	245	
	2.13	7.31	100	215	
	2.13	7.31	250	132	
	2.13	7.31	500	91	
Trifluoromethylbenzene	1.63	7.73	0	304	
	1.63	7.73	25	210	
	1.63	7.73	50	142	
	1.63	7.73	100	94	
	1.63	7.73	200	54.5	
	1.63	7.73	300	41	
	1.63	7.73	400	31	
1.63	7.73	500	27		
t-Butylbenzene	0.078 ± 0.005	7.83	0	376	
	0.078 ± 0.005	7.83	25	84	
	0.078 ± 0.005	7.83	50	54	
	0.078 ± 0.005	7.83	100	35	
	0.078 ± 0.005	7.83	200	21	
	0.078 ± 0.005	7.83	350	14.5	
	0.078 ± 0.005	7.83	500	13	
	0.078 ± 0.005	7.83	500	13	

^a Experiments with [¹⁴C]mesitylene; exchange rate corrected for radiation damage (see Table 2).

¹³ K. Coatsworth, E. Collinson, and F. S. Dainton, *Trans. Faraday Soc.*, 1960, **56**, 1008.

TABLE 8

Competition experiments with silver perchlorate
Reaction time = 5 days; tritium activity of water = 7.83 Ci dm⁻³

Substrate	10 ³ [Substrate]/M	10 ⁴ [AgClO ₄]/M	Exchange rate/ d.p.m. day ⁻¹ dm ³ Ci ⁻²
Benzene	3.45	0	546
	3.45	2.5	134
	3.45	5	91
	3.45	10	55
	3.45	20	35
	3.45	30	30
	3.45	40	24.5
	3.45	50	21.5
Toluene	3.11	0	548
	3.11	2.5	225
	3.11	5	145
	3.11	7.5	108
	3.11	20	62
	3.11	35	36
	3.11	50	32

TABLE 9

Competition experiments with nickel(II) sulphate
(Reaction time = 5 days)

Substrate	10 ³ [Substrate]/M	Tritium activity of water/ Ci dm ⁻³	10 ⁴ [NiSO ₄]/M	Exchange rate/ d.p.m. day ⁻¹ dm ³ Ci ⁻²
Chlorobenzene	1.54	7.32	0	394
	1.54	7.32	100	412
	1.54	7.32	200	305
	1.54	7.32	300	288
	1.54	7.32	400	432
	1.54	7.32	500	309
	Benzene	1.95	7.83	0
1.95		7.83	25	447
1.95		7.83	50	458
1.95		7.83	75	430
1.95		7.83	100	545
1.95		7.83	200	448
1.95		7.83	350	455
1.95		7.83	500	445
Mesitylene ^a		0.437	6.94	0
	0.437	6.94	100	387
	0.437	6.94	200	395
	0.437	6.94	300	413
	0.437	6.94	400	369
	0.437	6.94	500	489

^a Experiments with [¹⁴C]mesitylene; exchange rate corrected for radiation damage (see Table 2).

TABLE 10

Competition experiment, benzene *vs.* (copper + nickel) sulphates

[Benzene] = 4.94 × 10⁻³M; tritium activity of water = 7.75 Ci dm⁻³; reaction time = 5 days

[Copper sulphate]/M	[Nickel sulphate]/M	Exchange rate/ d.p.m. day ⁻¹ dm ³ Ci ⁻²
0.00	0.05	487
0.0025	0.0475	385
0.005	0.045	368
0.01	0.04	325
0.02	0.03	244
0.03	0.02	211
0.04	0.01	187
0.05	0.00	160

TABLE 11

Competition experiment, benzene *vs.* potassium iodide

[Benzene] = 2.98 × 10⁻³M; tritium activity of water = 7.73 Ci dm⁻³; reaction time = 4 days

[Potassium iodide]/M	Exchange rate/ d.p.m. day ⁻¹ dm ³ Ci ⁻²
0.00	504
0.005	381
0.01	324
0.02	320
0.03	303
0.04	297
0.05	284

TABLE 12

Competition experiment, toluene *vs.* methanol

[Toluene] = 1.88 × 10⁻³M; tritium activity of water = 7.73 Ci dm⁻³; reaction time = 7 days

[Methanol]/M	Exchange rate/ d.p.m. day ⁻¹ dm ³ Ci ⁻²
0.00	316
0.025	317
0.05	291
0.1	278
0.2	267
0.3	259
0.4	243

TABLE 13

Competition between benzene and mesitylene

[Mesitylene] = 2.45 × 10⁻⁴M; tritium activity of water = 6.94 Ci dm⁻³; reaction time = 7 days

10 ³ [Benzene]/M	Exchange rate for mesitylene/ d.p.m. day ⁻¹ dm ³ Ci ⁻² ^a	Exchange rate for benzene/ d.p.m. day ⁻¹ dm ³ Ci ⁻²	$k_{\text{Mesitylene}}/k_{\text{Benzene}}$
0	522		
0.69	356	134	7.5
1.38	264	221	6.7
2.07	211	266	6.7
2.76	187	296	7.1
3.10	186	297	8.0
3.45	161	326	6.8
			Mean 7.1

^a Experiments with [1,3,5-¹⁴C]mesitylene; results corrected for radiation damage (see Table 2).

TABLE 14

Competition between chlorobenzene and mesitylene

[Mesitylene] = 2.26 × 10⁻⁴M; tritium activity of water = 6.43 Ci dm⁻³; reaction time = 5 days

10 ³ [Chlorobenzene]/M	Exchange rate for mesitylene/ d.p.m. day ⁻¹ dm ³ Ci ⁻² ^a	Exchange rate for chlorobenzene/ d.p.m. day ⁻¹ dm ³ Ci ⁻²	$k_{\text{Mesitylene}}/k_{\text{Chlorobenzene}}$
0	560		
0.29	480	59	10.4
0.58	468	117	10.2
0.86	321	164	7.5
1.15	299	187	8.2
1.44	273	206	8.5
1.73	224	234	7.3
			Mean 8.7

^a Experiments with [1,3,5-¹⁴C] mesitylene; results corrected for radiation damage (see Table 2).

TABLE 15

Competition between toluene and benzonitrile

[Benzonitrile] = 1.95 × 10⁻³M; tritium activity of water = 7.75 Ci dm⁻³; reaction time = 7 days

10 ³ [Toluene]/M	Exchange rate for benzonitrile/ d.p.m. day ⁻¹ dm ³ Ci ⁻²	Exchange rate for toluene/ d.p.m. day ⁻¹ dm ³ Ci ⁻²	$k_{\text{Benzonitrile}}/k_{\text{Toluene}}$
0.00	460		
0.51	256	167	0.40
1.02	185	259	0.38
2.03	115	349	0.34
2.54	114	384	0.39
3.05	99	414	0.37
3.56	84	415	0.37
			Mean 0.37 ₅

TABLE 16

γ -Radiolysis: yield of labelled mesitylene as a function of dose

[Mesitylene] = 2.81×10^{-4} M; tritium activity of water = 7.31 Ci dm $^{-3}$; dose rate = 8.15 krad min $^{-1}$ = 1.36 J kg $^{-1}$ s $^{-1}$

Carbon-14		
Absorbed dose/ J kg $^{-1}$	activity of extract/ c.p.m.	Total 3 H activity/ d.p.m. ^a
0.00 ^b	452	193
203	371	6331
406	266	11,384
813	122	14,030

^a Figures refer to the total activity in the 25 cm 3 of reaction mixture and are *not* corrected for damage. ^b The tritium activity of this sample is due solely to β -radiolysis during the ca. 5 h between sample preparation and work-up.

TABLE 17

γ -Radiolysis: yield of labelled mesitylene as a function of mesitylene concentration

Tritium activity of water = 7.31 Ci dm $^{-3}$; dose rate = 1.69 J kg $^{-1}$ s $^{-1}$; total dose = 203 J kg $^{-1}$

Carbon-14		
$10^4 \times$ [Mesitylene]/ M	activity of extract/ c.p.m.	Total 3 H activity/ d.p.m. ^a
1.04	101	4302
2.07	225	4960
3.11	418	5965
4.15	586	6046
4.98	689	6632

^a These figures refer to the total activity in the 25 cm 3 of reaction mixture and are *not* corrected for damage.

TABLE 18

γ -Radiolysis: yield of labelled mesitylene as a function of copper(II) sulphate concentration

[Mesitylene] = 2.81×10^{-4} M; tritium activity of water = 7.31 Ci dm $^{-3}$; dose rate = 1.59 J kg $^{-1}$ s $^{-1}$; total dose = 190 J kg $^{-1}$

Carbon-14		
[Copper sulphate]/ M	activity of extract/ c.p.m.	Total 3 H activity/ d.p.m. ^a
0.00	365	6985
0.005	380	3296
0.010	405	2531
0.025	389	1838
0.050	328	578
0.00 ^b	421	

^a These figures refer to the total activity in the 25 cm 3 of reaction mixture and are corrected for damage but not referred to the standard tritium concentration 1.00 Ci dm $^{-3}$.

^b Zero-time sample for carbon-14 assay.

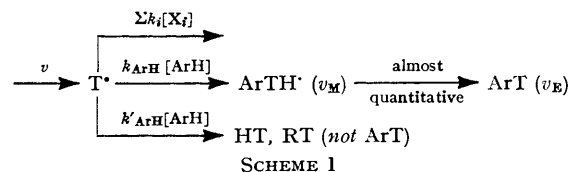
DISCUSSION

Radiation Damage.—Before a discussion of mechanistic and quantitative conclusions it is necessary to assess the complications introduced by radiation damage. We use this term to embrace all reactions of the solute under conditions which cause loss or chemical conversion of substrate into a form which is separated from the substrate during the isolation of a specimen for assay. The results of Tables 2 and 16 show that, for both β - and γ -radiolysis, damage increases with length of exposure, and those of Table 3 that the amount of material destroyed in β -radiolysis is essentially independent of the concentration of aromatic substrate. It follows from the latter result that the *percentage* of substrate lost as the result of radiation damage becomes less significant as the concentration of substrate in-

creases. For mesitylene the use of 14 C-labelled material leads to the required percentage corrections, which are quite small at the highest concentrations, such as those of the competition experiments reported in Tables 7, 9, and 13. For other solutes, for which double-labelling experiments were not performed, the concentration of substrate was generally much higher than in the case of mesitylene. On the assumption that these substances are not intrinsically more liable to radiation damage than mesitylene, we conclude that radiation damage for aromatic compounds at higher concentrations should only be of the order of 1–2%, and no correction for this slight loss of substrate was attempted.

By contrast, large amounts of radiation damage attended the γ -radiolyses, which related to a nearly 6000 times larger dose rate (8150 rad min $^{-1}$ = 1.355 J kg $^{-1}$ s $^{-1}$; as against 2.43×10^{-4} J kg $^{-1}$ s $^{-1}$ for typical β -radiolyses). Samples of mesitylene irradiated for more than five minutes were markedly turbid. By use of [14 C]mesitylene it was shown that a dose of 810 J kg $^{-1}$ gave a 75% reduction in the total carbon-14 activity of the extracted and purified mesitylene (Table 16). At the corresponding high concentration of damage-products (including phenol), these compete with mesitylene for tritium. Consequently the simple damage corrections are inapplicable in this case, and the high intensity γ -radiolysis is less amenable to quantitative kinetic study. Semi-quantitative results for the effects of substrate and scavenger concentration were nevertheless obtainable.

Reaction Mechanism.—On the basis of experiments with partially aerated solutions of mesitylene Adsetts and Gold² proposed Scheme 1 as the main mechanism of



the radiation-induced exchange. This involves radiolytic formation of aqueous tritium atoms (rate v), followed by their attack on the aromatic compound to form cyclohexadienyl radicals, the dominant fate of which is conversion into labelled mesitylene. The scavenging of the tritium atoms by the aromatic compound is in competition with other reactions, involving adventitious or deliberately added species.

It was concluded from previous work that scavenging by the aromatic compound which leads to labelled products other than ArT was relatively unimportant. More rigorously, the conclusion to be drawn from these experiments was that reaction products for the processes characterised by the rate constant k'_{ArH} were either negligible in amount or not separable from ArH. The present experiments, in which a wider range of chromatographic columns was used, reduces the likelihood of the second alternative. It has now been shown that the radioactivity of the ArH fraction did not include

a contribution from labelled cyclohexadienes. The scavenging processes characterised by $\Sigma k_i[X_i]$ include reaction with oxygen or other adventitious species as well as with species such as copper(II) ions which were added in some experiments as a controlled competitor for tritium atoms. The rate equation (1) which follows from Scheme 1 implies that, at sufficiently high concentrations of ArH, all tritium atoms would be de-

$$v_E \sim v_M = v \frac{k_{ArH}[ArH]}{(k_{ArH} + k'_{ArH})[ArH] + \Sigma k_i[X_i]} \quad (1)$$

stroyed by reaction with ArH (rate v_M) so that the rate of exchange (v_E) should reach a limiting value. Secondly, it implies a linear dependence of the ratio $[ArH] : v_E$ upon concentration of any one scavenger (the concentrations of other scavenger species being kept constant). Both these consequences of equation (1) appeared to be consistent with the experimental observations in our earlier work,² although the relatively low solubility of mesitylene did not permit the limiting rate to be reached at the highest concentrations attainable.

Equation (1) predicts that, if oxygen is present in the solution, the limiting rate should be reached at a higher concentration of ArH, since oxygen is very reactive towards hydrogen (and hence towards tritium) atoms ($k_{O_2} \sim 2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). It is therefore noteworthy that in the present work, where the residual concentration of oxygen is estimated to be in the region 10^{-7} – 10^{-6} M , the limiting rate is already attained almost at the lowest concentration of mesitylene employed (Table 3). From the previously determined rate constant for the reaction of mesitylene with tritium atoms (k_{ArH} ca. $10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) we estimate that for de-gassed solutions and a mesitylene concentration ($[ArH]$) of ca. $3 \times 10^{-4} \text{ M}$ the terms $k_{ArH}[ArH]$ and $k_{O_2}[O_2]$ in the denominator of the right-hand side of equation (1) are in a ratio between 100 : 1 and 1000 : 1, implying almost complete suppression of scavenging by oxygen as a result of de-gassing. On the other hand, the concentration of oxygen in air-saturated water is ca. $2.4 \times 10^{-4} \text{ M}$, and in such solutions the reaction with oxygen would be approximately as fast as the reaction with $3 \times 10^{-4} \text{ M}$ -mesitylene. These relative values thus explain why for the partially aerated solutions the rate of reaction of hydrogen atoms with mesitylene (at saturation concentration) is not large enough to make all other reactions negligible: the rate with oxygen is still of comparable magnitude. At lower concentrations of the aromatic compound, the reaction of hydrogen atoms with oxygen becomes the main reaction in partially aerated solutions.

G Values.—Because a true plateau was not reached in the earlier experiments on mesitylene in partially aerated solution, the estimate of the limiting rate previously derived³ is subject to some uncertainty. The value deduced³ (ca. 2800 d.p.m. per day of reaction

per dm^3 of solution at an activity of 3.6 Ci dm^{-3} corresponding to ca. 200 d.p.m. $\text{day}^{-1} \text{ dm}^3 \text{ Ci}^{-2}$) is to be compared with limiting rates in the region of 500–600 d.p.m. $\text{day}^{-1} \text{ dm}^3 \text{ Ci}^{-2}$ now obtained. Part of the discrepancy is ascribable to the incomplete suppression of oxygen competition even at the highest concentration of aromatic substrate. However, it seems unlikely that this is the sole reason: improved techniques of sample handling and the incursion of some electron-initiated exchange (see below) may also in part be responsible. When the electron-initiated exchange is suppressed (by addition of nickel sulphate) the limiting rate of exchange (via the tritium atom reaction) is estimated as 450 d.p.m. $\text{day}^{-1} \text{ dm}^3 \text{ Ci}^{-2}$. From the accepted G value for hydrogen atoms (0.6) and the average energy of tritium β -particles we calculate that 33.4 hydrogen atoms are formed per decomposition, or 1.07×10^{17} per day per dm^3 of solution containing 1 Ci dm^{-3} , of which 3.31×10^{10} are tritium atoms, if $G(T) = G(H)$. If all these were incorporated into benzene, then its total activity would be 3550 d.p.m. $\text{day}^{-1} \text{ dm}^3$. The ratio 3550 : 450 (expected activity : observed activity) is our estimate of the isotope effect on G , i.e. $G(H)/G(T) = 8 \pm 2$. This may be compared with Anbar and Meyerstein's estimate¹⁴ of 4.8 ± 0.9 , calculated from experimental data due to Dyne *et al.*¹⁵

γ -Radiolysis of mesitylene solutions at comparatively low total doses (203 J kg^{-1}) and low radiation damage established that here too the amount of hydrogen exchange in mesitylene increased with substrate concentration (Table 17), seemingly towards a plateau, the value for $5 \times 10^{-4} \text{ M}$ -mesitylene being ca. 90% of that for a corresponding β -radiation dose.

Scavenger Effects.—Equation (1) has been used to deduce relative rate constants for different hydrocarbons ArH by observation of the rate reduction brought about by addition of a scavenger [*e.g.* copper(II) ion]. The appropriately rearranged form of equation (1) for copper(II) inhibition is (2), where the sum in the final term no longer includes the contribution of copper(II)

$$\frac{[ArH]}{v_E} = \frac{k_{Cu}[Cu^{2+}]}{vk_{ArH}} + \left\{ \frac{(k_{ArH} + k'_{ArH})[ArH]}{vk_{ArH}} + \frac{\Sigma k_i[X_i]}{vk_{ArH}} \right\} \quad (2)$$

ion which has been separated as the first term of the right-hand side. Provided that the final term remains constant during a series of experiments in which the concentration of copper(II) is varied, the determination of the ratio $k_{Cu} : vk_{ArH}$ from equation (2) (for example by plotting $[ArH]/v_E$ against $[Cu^{2+}]$) should be valid irrespective of whether the last term is large or small. It follows that the presence or absence of oxygen should not affect relative reactivities evaluated by this procedure and the repetition, with de-gassed solutions, of Adsetts

¹⁴ M. Anbar and D. Meyerstein in 'The Radiation Chemistry of Aqueous Systems,' ed. G. Stein, Weizmann Science Press of Israel, Jerusalem, 1968.

¹⁵ P. J. Dyne, R. W. Fletcher, W. M. Jenkinson, and I. P. Ray, *Canad. J. Chem.*, 1961, **39**, 933.

and Gold's measurements on copper(II) ions and benzene and mesitylene should still lead to the same answers.

For partially aerated solutions, the graph of $[\text{ArH}]/v_{\text{E}}$ against $[\text{Cu}^{2+}]$ was of the linear form required by equation (2). However, for de-gassed solutions the first point or points on the graph (corresponding to reaction in the total absence or at very low concentrations of copper salt) fell almost invariably off the line. The rate depression by low concentrations of the scavenger was much more marked than that at higher concentrations (see for example, Figure 1). After the low-concentration curvature the graphs were linear, with slopes in good agreement with those observed in earlier work with partially aerated solutions. These features of the

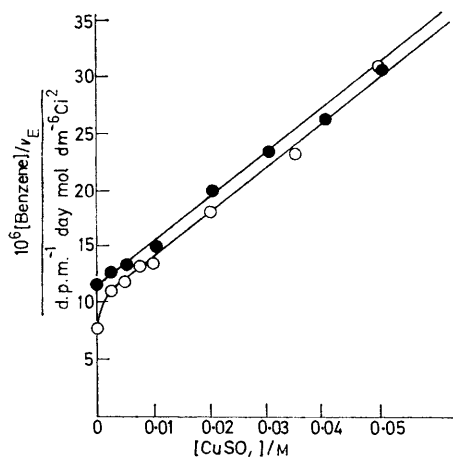
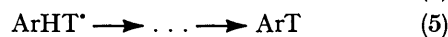


FIGURE 1 Competition plot: benzene exchange in the presence of copper(II) sulphate [equation (2)]: open circles, copper(II) sulphate alone; filled circles, $([\text{CuSO}_4] + [\text{NiSO}_4] = 0.05\text{M})$

copper(II) inhibition of exchange suggest that low concentrations of this scavenger or dissolved oxygen can eliminate an exchange pathway which is available only in the de-gassed solutions in the absence of copper(II) salt.

One possibility is that the additional exchange represents the formation of an impurity which readily exchanges hydrogen with the solvent and which is not separated from the aromatic substrate by the normal gas-chromatographic procedure, and that formation of this product is totally suppressed in the presence of copper(II) or oxygen. In view of the further improvement in our separation technique this hypothesis is unattractive.

A more likely explanation of the 'additional' exchange route is that it represents exchange by the reaction sequence (3)–(5). It is known¹⁶ that these



reactions are the main exchange route in the absence

¹⁶ M. H. Studier and E. J. Hart, *J. Amer. Chem. Soc.*, 1969, **91**, 4068.

of hydrogen atoms. This route is suppressed by oxygen and also by copper(II) ions since both these species are much more reactive towards solvated electrons than benzene is. From the known rate constants for the reactions of copper(II) ions and aromatic compounds with hydrogen atoms and electrons ($k^{\text{H}_{\text{Cu}}} = 6 \times 10^8 \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3$ and $k^{\text{e}_{\text{Cu}}} = 4 \times 10^{10} \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3$)⁴ we can deduce that the electron-induced aromatic exchange will be inhibited by much lower concentrations of copper(II) sulphate than the hydrogen atom-induced exchange. In the presence of 0.01M-Cu^{2+} the former is cut to 1% of its value in the absence of scavengers, whereas the latter is reduced by only about one half. We can thus account for the excessive rate in scavenger-free solution. It also follows that we can use equation (2) and practically neglect the incursion of the electron-induced reaction, provided attention is confined to results for copper(II) sulphate concentrations greater than 0.01M . In our earlier experiments² the presence of oxygen would have precluded the detection of this effect since 99% of the available electrons would have reacted with $2 \times 10^{-4}\text{M}$ -oxygen instead of with 10^{-3}M -benzene. In the presence of *ca.* 10^{-6}M -oxygen (the estimated concentration of the present experiments), only *ca.* 50% of electrons are removed by oxygen, and hence their effect is detectable. For silver ions, the rate constants for reaction with electrons and with hydrogen atoms are nearly identical (3.2×10^{10} and $4 \times 10^{10} \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3$ respectively).^{17,18} This accounts for the observation that inhibition plots for silver ions based on equation (2) are curved over a wider range than those with copper(II) ions. On this interpretation, linear inhibition plots with silver ions should be obtainable in solutions containing some dissolved oxygen to act as electron scavenger. Such experiments have not so far been carried out.

Support for this reaction model, involving electron-induced exchange as a contributory exchange route in de-gassed solutions, comes from the observation that nickel sulphate (which exerts no effect on the exchange in partially aerated solutions)² causes a slight reduction of the exchange rate at quite low concentrations (Table 9). No further reduction in benzene exchange occurs at nickel concentrations above 0.0025M , when the electron-induced reaction is fully suppressed.

A series of experiments was carried out with benzene solutions containing varying amounts of nickel sulphate and copper sulphate such that their combined concentration was constant (0.05M) (Table 10). Copper(II) and nickel(II) ions have practically the same reactivity towards solvated electrons. Accordingly the electron-initiated exchange should be suppressed for all compositions, and the progressive decrease of the exchange reaction with increasing copper(II) concentration should reflect only hydrogen atom scavenging. Within the limits of experimental error the inhibition plot with

¹⁷ M. S. Matheson, W. A. Mulac, J. L. Weeks, and J. Rabani, *J. Phys. Chem.*, 1966, **70**, 2092.

¹⁸ E. Hayon and J. Moreau, *J. Chim. phys.*, 1965, 391.

respect to copper(II) ion (see Figure 1) is now linear, with a slope equal to that of the linear portion of the inhibition plot with copper sulphate alone.

Because of the low rate of reaction of solvated electrons with hydrogen ion or water in neutral solution,⁴ one may disregard the possibility that some hydrogen (tritium) atoms in our system are derived from this process.

Marked copper(II) inhibition of exchange was also observed for γ -radiolyses, thus supporting the basic interpretation of the radiation-chemical mechanism (Table 18), but it was not examined in detail, in view of the importance of radiation damage in these experiments.

The Fate of Cyclohexadienyl Radicals in Aqueous Solution.—The observation that labelled cyclohexadienes are not formed under conditions where hydrogen (tritium) atom addition is responsible for the initiation of the exchange, suggests that a bimolecular radical-radical disproportionation into equimolar amounts of aromatic compound and cyclohexadiene is not a significant route for product formation under our conditions. This contrasts with the conclusions reached for pulse-radiolytically generated cyclohexadienyl radicals which were found to decay according to a second-order rate law¹⁹ with a rate constant of $1.8 \times 10^9 \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3$. Studier and Hart thus account for the formation of cyclohexadiene and of biphenyl derivatives by disproportionation* and pairwise combination of cyclohexadienyl radicals in the γ -radiolysis of alkaline aqueous solutions of benzene saturated with hydrogen under high pressure.¹⁶ However, there is a big difference between these experiments and ours. First, the irradiation intensity in our β -radiolyses was of the order of 10^3 times lower than that in Studier and Hart's γ -radiolyses, and the stationary concentration of radicals (and hence the rate of bimolecular radical-radical reactions) should therefore be reduced by a similar factor. On the other hand, the difference in L.E.T. values between different forms of radiation²¹ and the picture that the energy of β -radiation is deposited in short tracks rather than in isolated spurs (with a consequently increased local concentration of radicals) could be advanced as possible arguments against this conclusion. A further difference is the presence of oxidising agents in many of our experiments.

From the known or estimated rate constants of various reactions of the cyclohexadienyl radical it is possible to calculate the relative importance of alternative routes for its disappearance and hence to deduce the dominant mechanism operating under the conditions of our experiments, as follows.

* Disproportionation may be initiated by electron disproportionation:



¹⁹ M. C. Sauer, jun., and B. Ward, *J. Phys. Chem.*, 1967, **71**, 3971; B. D. Michael and E. J. Hart, *J. Phys. Chem.*, 1970, **74**, 2878.

²⁰ H. R. Haysom, J. M. Phillips, and G. Scholes, *J.C.S. Chem. Comm.*, 1972, 1082.

Four modes of destruction of cyclohexadienyl radicals are considered.

(i) Unimolecular decomposition, estimated from gas-kinetic results²² [$k_{\text{uni}} = 3 \times 10^{13} \exp(-31,000/1.986T)$] to have a first-order rate constant of $6 \times 10^{-10} \text{ s}^{-1}$ at 25°. (ii) Second-order radical-radical reactions¹⁹ (sum of dimerisation and disproportionation) have an overall rate constant $k_{\text{bi}} = 1.8 \times 10^9 \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3$. (iii) Reaction with oxygen: the second-order rate constant for the reaction of the hydroxycyclohexadienyl radical with oxygen²³ ($5 \times 10^8 \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3$) is thought to be a fair approximation. In de-gassed solutions the concentration of oxygen is *ca.* 10^{-6} M . (iv) Reaction with copper(II) ion is expected to have a second-order rate constant (k_{c}) of at least $10^8 \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3$ by analogy with results for alkyl radicals.²⁴

An upper limit to the stationary concentration of cyclohexadienyl radicals can now be obtained by equating their rate of formation with the rate of destruction by modes (i)–(iii). [The stationary concentration will evidently be lower if the route (iv) also contributes to the destruction of the radicals.] An upper limit for the rate of formation of cyclohexadienyl radicals is given by the rate of radiolytic formation of hydrogen atoms (which would apply if every hydrogen atom were captured by benzene with formation of a cyclohexadienyl radical). If we assume that the *G* value for formation of hydrogen atoms by ⁶⁰Co γ -radiation²⁵ (0.6) is applicable to tritium β -radiolysis (*cf.* ref. 21), the rate of formation of hydrogen atoms in tritiated water containing 8 Ci dm^{-3} will be given by $(8 \times 3.7 \times 10^{10} \times 5560 \times 0.6/100 \times 6.02 \times 10^{23}) \text{ s}^{-1} \text{ mol} \text{ dm}^{-3} = 1.64 \times 10^{-11} \text{ s}^{-1} \text{ mol} \text{ dm}^{-3}$ where 5560 eV is the average energy of the tritium β -particle. Equating this rate of formation with the rate of loss by modes (i)–(iii), we obtain $[\text{ArH}_2\cdot] = 3 \times 10^{-14} \text{ M}$.

The relative contributions to the destruction of cyclohexadienyl radicals in de-gassed solutions (with $[\text{O}_2] = 10^{-6} \text{ M}$) in the absence of copper(II) ions, are therefore as follows: (i) unimolecular decomposition: $v = k_{\text{uni}} [\text{ArH}_2\cdot] = 1.8 \times 10^{-23} \text{ s}^{-1} \text{ mol} \text{ dm}^{-3}$; (ii) bimolecular decomposition: $v_{\text{bi}} = k_{\text{bi}} [\text{ArH}_2\cdot]^2 = 1.6 \times 10^{-18} \text{ s}^{-1} \text{ mol} \text{ dm}^{-3}$; and (iii) reaction with oxygen: $v_{\text{ox}} = k_{\text{ox}} [\text{ArH}_2\cdot][\text{O}_2] = 1.5 \times 10^{-11} \text{ s}^{-1} \text{ mol} \text{ dm}^{-3}$.

Accordingly, reaction with oxygen far outweighs the alternative processes, and this should be true even if the oxygen concentration were further reduced by several powers of ten. (In Studier and Hart's

²¹ A. Appleby and H. A. Schwarz, *J. Phys. Chem.*, 1969, **73**, 1937; M. Anbar in 'Fundamental Processes in Radiation Chemistry,' ed. P. Ausloos, Interscience, New York, 1968; E. Collinson, F. S. Dainton, and J. Kroh, *Proc. Roy. Soc.*, 1961, **A**, **265**, 422; A. Appleby and W. F. Gagnon, *J. Phys. Chem.*, 1971, **75**, 601.

²² D. G. L. James and R. D. Suart, *Trans. Faraday Soc.*, 1968, **64**, 2752.

²³ L. M. Dorfman, I. A. Taub, and R. E. Buhler, *J. Chem. Phys.*, 1962, **36**, 3051.

²⁴ J. K. Kochi and R. V. Subramanian, *J. Amer. Chem. Soc.*, 1965, **87**, 4855.

²⁵ G. Scholes and M. Simic, *Nature*, 1963, **199**, 276; D. C. Walker, *Quart. Rev.*, 1967, **21**, 79.

experiments, with a much higher rate of irradiation *and* more scrupulous measures of oxygen removal, it is quite understandable that the bimolecular reactions should be very much more important.) Of course, these calculations apply only to the situation at the start of irradiation, before oxygen has been consumed by reaction (iii).

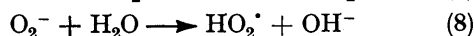
In the presence of copper(II) ions in quite low concentrations, reaction of cyclohexadienyl radicals with copper(II) ions is at all stages more important than the reaction with oxygen. The product $k_0[\text{Cu}^{2+}]$ in a 10^{-2}M solution of Cu^{2+} has a value of at least 10^6 s^{-1} , whereas the product $k_{ox}[\text{O}_2]$ in our solutions is, according to the values given above, $5 \times 10^2 \text{ s}^{-1}$. As a result, the stationary concentration of $\text{ArH}_2\cdot$ radicals in the presence of Cu^{2+} ions is *ca.* 1000 times lower than in their absence.

The foregoing calculations of the relative importance of alternative reactions of the cyclohexadienyl radical are open to the criticism that the local concentration of radicals controlling their rate of bimolecular reaction may be higher than the bulk concentration used. If this is important, then we have underestimated the role of the bimolecular path in comparison with the other reactions by a factor which we cannot quantify. However, this is unlikely to approach the factor of $>10^{10}$ by which, according to our calculation, the reaction with 0.01M-copper(II) ion predominates over the bimolecular reaction.

As for the reactions of aliphatic radicals with copper(II) ions,²⁴ the reaction of the cyclohexadienyl radical with copper(II) ion is thought to be one of electron transfer (6), which is followed by proton loss.

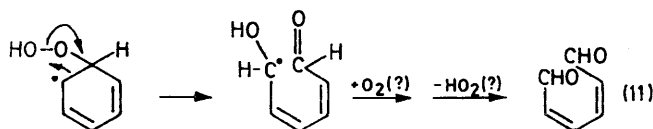
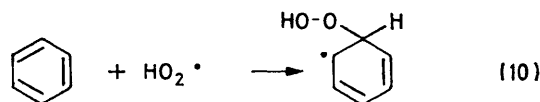


In partially deoxygenated solution most of the cyclohexadienyl radicals revert to the original aromatic compound. This reaction may either involve a similar electron transfer (7) and subsequent protonation of O_2^- (8) and proton loss from the cyclohexadienyl cation, or direct hydrogen atom transfer (9).



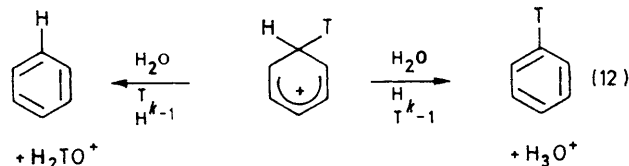
It is reported that the radiolysis of benzene in aerated aqueous solutions gives rise to phenol,^{26,27} mucondialdehyde (hexa-2,4-dienedial)²⁶ and β -hydroxymucondialdehyde.²⁷ The intervention of hydroperoxyl radicals (10) provides a reasonable route to the formation of mucondialdehyde. Reaction (10) can be followed either by ring cleavage and hydrogen loss (11) or by electron

transfer and subsequent ring cleavage. The formation of β -hydroxymucondialdehyde²⁷ in solutions of benzene with substantial radiation damage is correspondingly



seen as the consequence of the reaction of the hydroperoxyl radical at the *para*-position of phenol (which is always present in such solutions, probably as a result of hydroxyl radical attack on benzene). These routes for the formation of aldehydic radiation damage products may be more plausible and simpler than other proposed mechanisms.^{23,28}

Isotope Effects.—If, as is suggested above, the final step of the exchange is in most cases a proton transfer (and not a hydrogen atom transfer), then the isotope effects of electrophilic hydrogen isotope exchange reactions can be used to estimate the relative importance of the two isotopically different modes of breakdown of the intermediate, *i.e.* process (12). The difference



between the rate of formation of the intermediate (v_M) and the rate of its breakdown (or exchange, v_E) is accordingly given by (13).

$$v_E = v_M \cdot \frac{\frac{\text{H}k_{-1}}{\text{T}k_{-1}}}{\frac{\text{H}k_{-1}}{\text{T}k_{-1}} + \frac{\text{T}k_{-1}}{\text{H}k_{-1}}} = v_M / (1 + \frac{\text{T}k_{-1}}{\text{H}k_{-1}}) \quad (13)$$

For 1,3,5-trimethoxybenzene the intramolecular isotope effect $\frac{\text{H}k_{-1}}{\text{T}k_{-1}}$, favouring proton loss over triton loss,²⁹ is of the order of 20, which implies that *ca.* 95% of the reaction proceeds in the direction of tritium incorporation. For protodeuteriation the corresponding isotope effect is known to vary with the reactivity of the aromatic compound.³⁰ For the less reactive aromatic compounds (such as benzene) the tritium isotope effect, calculated from the deuterium isotope effect by use of the exponent³¹ 1.442, may be as low as 7, corresponding to 88% tritium incorporation. For

²⁶ G. Stein and J. J. Weiss, *J. Chem. Soc.*, 1949, 3245.

²⁷ T. K. K. Srinivasan, I. Balakrishnan, and M. P. Reddy, *J. Phys. Chem.*, 1969, **73**, 2071.

²⁸ I. Balakrishnan and M. P. Reddy, *J. Phys. Chem.*, 1970, **74**, 850.

²⁹ A. J. Kresge and Y. Chiang, *J. Amer. Chem. Soc.*, 1967, **89**, 4411; see also B. D. Batts and V. Gold, *J. Chem. Soc.*, 1964, 4284.

³⁰ L. Melander and S. Olsson, *Acta Chem. Scand.*, 1956, **10**, 879; B. Östman and S. Olsson, *Arkiv Kem.*, 1960, **15**, 275; S. Olsson, *ibid.*, 1960, **16**, 482; 1970, **32**, 105; A. J. Kresge, *Discuss. Faraday Soc.*, 1965, **39**, 49; J. L. Longridge and F. A. Long, *J. Amer. Chem. Soc.*, 1967, **89**, 1292.

³¹ C. G. Swain, E. C. Stivers, J. F. Reuwer, and L. J. Schaad, *J. Amer. Chem. Soc.*, 1958, **80**, 5885.

the compounds covered in the present study, this percentage is probably confined to the range between 85 and 91%. The reactivity ratios based on tritium exchange therefore differ by probably not more than $\pm 3\%$ from the relative reactivities for hydrogen atom addition.

These estimates are based on heterolytic loss of cationic hydrogen from a carbonium ion. However, should the foregoing mechanism for the conversion of cyclohexadienyl radicals to aromatic compound be in error and the process be a direct hydrogen atom transfer, then these calculations would not be applicable. Even in that case, however, the primary isotope effect is expected predominantly to favour protium loss over tritium loss, with only a narrow range of values for the percentage of formation of tritium-labelled aromatic compound from tritium-labelled cyclohexadienyl radical.

Comparison of the exchange inhibition by copper(II) sulphate for mesitylene and [2,4,6- $^2\text{H}_3$]mesitylene leads to the conclusion that the deuterated compound is *ca.* 1.5 ± 0.2 times less 'reactive'. In considering the significance of this difference it is important to note that our comparison of reactivities for different compounds is based on the above conclusion that the rate of exchange is a fairly constant fraction (85–91%, according to the preceding paragraphs) of the rate of tritium addition. However, this fraction will be lower for tritium exchange into a deuterated compound, because the intramolecular primary isotope effect discriminates less between deuterium and tritium loss from the deuterated cyclohexadienyl intermediate than between protium and tritium loss in the case of the ordinary compound. If the final step of the exchange involves the competition between the two reactions of equation (12), then the ratio of the tritium exchange rates into mesitylene and [$^2\text{H}_3$]mesitylene (v_{B}^{H} and v_{B}^{D}) will, according to equation (13) be given by (14) [where the symbols $\frac{\text{T}}{\text{D}}k_{-1}$ and $\frac{\text{D}}{\text{T}}k_{-1}$ are defined

$$v_{\text{B}}^{\text{H}}/v_{\text{B}}^{\text{D}} = (1 + \frac{\text{T}}{\text{D}}k_{-1}/\frac{\text{D}}{\text{T}}k_{-1}) / (1 + \frac{\text{T}}{\text{H}}k_{-1}/\frac{\text{H}}{\text{T}}k_{-1}) \quad (14)$$

by analogy with the definitions of $\frac{\text{H}}{\text{T}}k_{-1}$ and $\frac{\text{T}}{\text{H}}k_{-1}$ in equation (12)]. From the relation (15) it can then

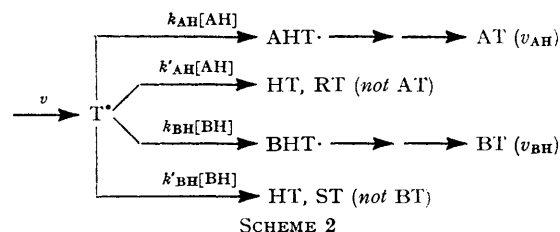
$$(\frac{\text{T}}{\text{D}}k_{-1}/\frac{\text{D}}{\text{T}}k_{-1}) = (\frac{\text{T}}{\text{H}}k_{-1}/\frac{\text{H}}{\text{T}}k_{-1})^{0.442/1.442} \quad (15)$$

be calculated that the isotope effect expressed in equation (14) should be *ca.* 1.34–1.37, if the ratio $\frac{\text{H}}{\text{T}}k_{-1}/\frac{\text{T}}{\text{H}}k_{-1}$ is in the region 5–10. This is in fair agreement with the experimental ratio $v_{\text{B}}^{\text{H}}/v_{\text{B}}^{\text{D}} = 1.5 \pm 0.2$. In going from equation (13) to (14) we assumed that there is no isotope effect on v_{M} . Whilst this may not be strictly correct, the error introduced would not exceed *ca.* 10% of the value of the isotope effect, which is within the error limits for this derived quantity.

Reactivity Comparisons by Competition with Copper(II) Sulphate.—The main series of reactivity comparisons is based on the effectiveness of exchange inhibition by copper(II) ions. The linear portion of a graph of $[\text{ArH}]/v_{\text{B}}$ against $[\text{Cu}^{2+}]$ has, according to equation (2), a slope of

$k_{\text{Cu}}/vk_{\text{ArH}}$. For comparative experiments on a series of aromatic compounds, the ratio $k_{\text{Cu}}:v$ is constant, so that the slopes should be in the inverse ratio of the rate constants for tritium attack. The evaluation of these relative reactivities is not always straightforward because the curved portion of the graph, at low concentrations of copper sulphate, has to be ignored for reasons which have already been discussed, and because the low activities (*i.e.* values of v_{B}) found for solutions at very high copper(II) ion concentrations reduce the precision of $[\text{ArH}]/v_{\text{B}}$. Hence the position of the 'best' straight line through the points is in some cases not quite free from subjective judgement, and the experimental results are therefore tabulated in full. In the summary of rate comparisons (Table 19), the value for *t*-butylbenzene is the least securely established one. It is conceivable that the true reactivity ratio may in fact be as low as 1.8. Even this value is considerably larger than the relative reactivities towards phenyl and trifluoromethyl radicals, as shown in Table 19. The difference is intelligible on steric grounds since attack at *ortho*-positions is blocked for large radicals but may be possible for tritium atoms.

Aromatic Reactivity Comparisons by Direct Competition.—As a cross-check on the reactivity comparisons *via* copper sulphate three experiments were performed in which the exchange in one aromatic substrate (AH) was inhibited by a second aromatic substrate (BH) (Tables 13–15). The concentration of aromatic compounds in these experiments was high so that scavenging of hydrogen atoms by other species can be neglected. The situation is represented by Scheme 2. The com-



petition law for this Scheme, analogous to equation (2) is given in equations (16) and (17), and its validity is

$$\frac{[\text{AH}]}{v_{\text{AH}}} = \frac{(k_{\text{AH}} + k'_{\text{AH}})[\text{AH}]}{vk_{\text{AH}}} + \frac{(k_{\text{BH}} + k'_{\text{BH}})[\text{BH}]}{vk_{\text{AH}}} \quad (16)$$

$$\frac{[\text{BH}]}{v_{\text{BH}}} = \frac{(k_{\text{AH}} + k'_{\text{AH}})[\text{AH}]}{vk_{\text{BH}}} + \frac{(k_{\text{BH}} + k'_{\text{BH}})[\text{BH}]}{vk_{\text{BH}}} \quad (17)$$

illustrated in Figure 2. It also follows, for example by dividing equation (17) by equation (16), that, in any one exchange experiment, equation (18) holds. Reactivity ratios calculated in this way from the individual experiments are included in Tables 13–15. Table 20 compares these results with those deduced from the

$$\frac{v_{\text{AH}}[\text{BH}]}{v_{\text{BH}}[\text{AH}]} = \frac{k_{\text{AH}}}{k_{\text{BH}}} \quad (18)$$

copper sulphate inhibition experiments. Equations

(18) and (19) respectively predict that on plotting either $[AH]/v_{AH}$ or $[AH]/v_{BH}$ against $[AH]$ the ratio of extrapolated intercept : slope should equal $[BH](k_{BH} + k'_{BH})/(k_{AH} + k'_{AH})$. The final two columns of Table 20 list

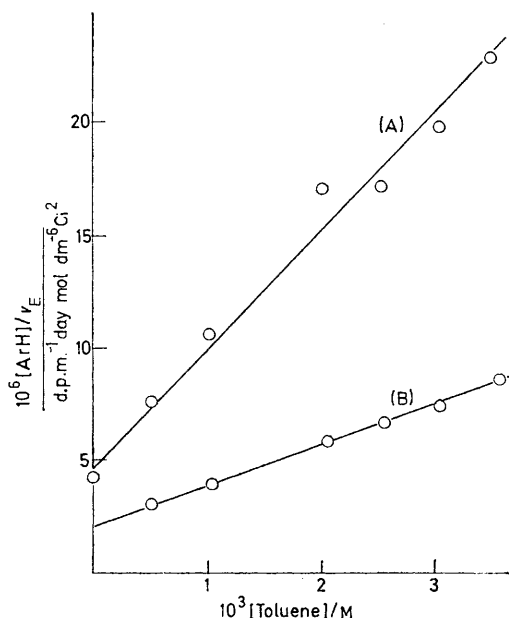
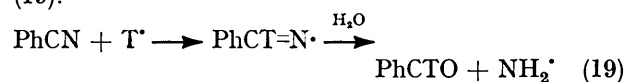


FIGURE 2 Competition plots: benzointrile (A)—toluene (B) system [equations (16) and (17)]

the ratios $(k_{BH} + k'_{BH})/(k_{AH} + k'_{AH})$ deduced in this manner from the two graphs. As can be judged from the scatter of

agreement of k_{BH}/k_{AH} by the two methods. However, the precise size of the electron-induced contribution depends, on the reasoning given before, on the concentration of residual oxygen in the solution, which is bound to be slightly variable. It is also thought that errors in substrate concentrations can be more serious in experiments with two volatile solutes, since evaporation of the first substrate may occur during the addition of the second. The results obtained by the direct method are therefore regarded only as confirmatory evidence concerning the general conclusions. The approximate agreement between k_{BH}/k_{AH} and $(k_{BH} + k'_{BH})/(k_{AH} + k'_{AH})$ in the case of the benzene-mesitylene comparison again supports the earlier conclusion³ regarding the relative unimportance of the rate constants k'_{AH} and k'_{BH} . The results for the chlorobenzene-mesitylene system suggest that k'_{AH} may be significant for chlorobenzene, as is also indicated by the formation of labelled benzene from chlorobenzene.³² A similar discrepancy in the toluene-benzointrile experiment is not due to benzene formation from benzointrile as this reaction is relatively unimportant.³² We tentatively ascribe it to formation of benzaldehyde by the route³³ (19).



Reactivity Comparisons of Scavengers.—The effectiveness of different scavengers in reducing the exchange in an aromatic compound can be used to determine their relative reactivities towards tritium atoms, and

TABLE 19
Relative rate constants ($k_{ArX}/k_{Benzene}$) of aromatic compounds towards reactive species

Substrate	Reactive species							$10^{-\sigma_p}$
	T ^a	H ^b	CF ₃ ^c	Ph ^d	CHCO ₂ Et ^e	NCO ₂ Et ^e	HcT ^f	
Benzene	(1)	(1)	(1)	(1)	(1)	(1)	(1)	1.0
Toluene	2.2	<i>2.4, 2.7</i>	1.6	1.2	1.06	2.06	1.5	1.5
Anisole	2.7	1.5	2.8	2.0	1.15	2.88	3.0	1.9
Mesitylene	8.5		5.8					
Fluorobenzene	1.0	0.7	0.5	1.0	0.80	0.62	1.2	0.87
Chlorobenzene	1.1	1.3	0.6	1.1	0.84	0.77	1.6	0.59
Bromobenzene	1.1		0.8	1.3			2.0	0.59
Trifluoromethylbenzene	0.35	0.6	0.3		0.55	0.22	0.8	0.29
t-Butylbenzene	3.8		0.9	0.64				1.6
Benzointrile	0.9	<i>0.6, 0.4, 0.54</i>	0.4	3.7		0.55	2.2	0.22

^a Based on Cu(II) inhibition. ^b Italicised values in this column refer to aqueous solution,^{5,19} others to gas-phase experiments.⁶ ^c In 2,2,4-trimethylpentane solution (I. M. Whittemore, A. P. Stefani, and M. Szwarc, *J. Amer. Chem. Soc.*, 1962, **84**, 3799). ^d From thermolysis of benzoyl peroxide in mixed aromatic medium. (For results and references see D. H. Hey, *Adv. Free Radical Chem.*, 1967, **2**, 47; G. H. Williams, 'Essays on Free Radical Chemistry,' Chem. Soc. Special Publ. No. 24, 1970, p. 25). ^e Thermolytically generated in an unreactive perfluorinated polyether.³⁸ ^f From decay of T₂. Results approximate.³⁷

points in Figure 2, these values are probably uncertain to the extent of ± 10 –20%. For various reasons, the other results given in Table 20 are less precise than the reactivity ratios obtained *via* the copper sulphate competition. The direct reactivity comparisons suffer from the drawback that the exchange values in the absence of added electron scavengers include a contribution from the electron-induced exchange reaction. This appears to be small, in view of the fair linearity of inhibition plots, such as those in Figure 2, and the approximate

to relate these reactivities to that of benzene and those of other aromatic compounds. The basis of these comparisons is an analogue of equation (2). At high concentrations of the aromatic compound (so that tritium atom scavenging by species other than by the aromatic substrate ArH and by the deliberately added

³² C. L. Brett and V. Gold, *Chem. Comm.*, 1971, 1426.
³³ Cf. M. Anbar, *Adv. Phys. Org. Chem.*, 1969, **7**, 126; P. Neta and R. W. Fessenden, *J. Phys. Chem.*, 1970, **74**, 3362; J. P. Ferris and F. R. Antonucci, *Chem. Comm.*, 1971, 1294.

scavenger S is negligible), the inhibition equation can be written as (20). The ratio (extrapolated intercept):

$$\frac{[\text{ArH}]}{v_{\text{E}}} = \frac{k_{\text{S}}[\text{S}]}{vk_{\text{ArH}}} + \frac{(k_{\text{ArH}} + k'_{\text{ArH}})[\text{ArH}]}{vk_{\text{ArH}}} \quad (20)$$

slope, for a graph of $[\text{ArH}]/v_{\text{E}}$ against $[\text{S}]$, should equal $(k_{\text{ArH}} + k'_{\text{ArH}})[\text{ArH}]/k_{\text{S}}$ or, when k'_{ArH} is known to be negligible as in the case of benzene and methylbenzenes, it should equal $k_{\text{ArH}}[\text{ArH}]/k_{\text{S}}$. The procedure is valid for those tritium atom scavengers which have a high reactivity towards solvated electrons, so that the linear portion of the inhibition graph relates solely to competition between ArH and S for tritium atoms. When this is not true equation (1) must be replaced by a two-term equation, the second term of which relates to exchange by the route of equations (3)—(5).

of rate constants for other scavengers, we are probably placing excessive reliance on the precision with which k_{Cu}^{H} is known. Baxendale *et al.*³⁵ have reported values for this rate constant which are over ten times smaller than the value used in Table 21. The complete neglect of isotope effects in these comparisons may also not be justified. Perfect agreement between k_{S}^{H} and k_{S}^{T} values cannot therefore be expected.

Aromatic Reactivity.—Table 19 lists relative rate constants (values of k_{ArH}) derived from the copper(II)-inhibition studies (considered to be the most reliable reactivity comparisons, $\pm 20\%$, of the present series of experiments) by use of equation (2). The results refer to the sum of tritium-for-hydrogen replacement reactions occurring for each compound. If expressed per exchanging position, the figures would be somewhat

TABLE 20
Reactivity comparisons by different competition procedures

AH	BH	$k_{\text{BH}}/k_{\text{AH}}$		$\frac{k_{\text{BH}} + k'_{\text{BH}}}{k_{\text{AH}} + k'_{\text{AH}}}$	
		<i>via</i> CuSO ₄ (Table 19)	Direct (Tables 13—15)	[From equation (16)]	[From equation (17)]
Benzene	Mesitylene	8.5	7.1	7.5	7.0
Chlorobenzene	Mesitylene	7.4	8.7	5.5	6.5
Toluene	Benzonitrile	0.41	0.375	0.60	0.47

Since the corresponding complete inhibition law is too complex for application to our limited data, we do not detail this development and have based our comparison of the effects of different scavengers on equation (20). Relative values of k_{S} have been evaluated [with reference to Cu^{II} ion as standard] as shown in Table 21.

TABLE 21

Rate constants for the reaction of hydrogen (tritium) atoms with various scavengers

S	$k_{\text{S}}^{\text{T}}/k_{\text{Cu}}^{\text{T}}$	$10^7 k_{\text{S}}^{\text{T}^a}$	$10^7 k_{\text{S}}^{\text{H}^b}$	Reference
Copper(II) ion	(1.0)		60	18, 34
Benzene	5.0	300	110, 58	19, 20
Silver(I) ion	68	4100	4000, 1150	4, 18
Iodide ion	0.092	5.5	4.0, 53	<i>c</i>
Methanol	0.0081	0.48	0.16	23, 34, 35, ^d

^a Calculated on the assumption that the value for k_{Cu}^{H} (taken from the literature^{18,34}) also applies to k_{Cu}^{T} . ^b Literature values; references in final column. ^c Z. D. Draganić and I. G. Draganić, *J. Phys. Chem.*, 1972, **76**, 2733; R. Hentz and C. Johnson, *J. Chem. Phys.*, 1969, **51**, 1236. ^d G. Scholes and M. Simic, *J. Phys. Chem.*, 1964, **68**, 1731, 1738; J. Rabani, *J. Amer. Chem. Soc.*, 1962, **84**, 868.

Where comparison with other data is possible, the agreement is fair and suggests that the neglect of the electron-induced path is justified for experiments corresponding to the linear portions of the inhibition plots.

By taking a selected literature value for the absolute rate for the copper(II) ion as the basis for the calculation

³⁴ A. Appleby, G. Scholes, and M. Simic, *J. Amer. Chem. Soc.*, 1963, **85**, 3891.

³⁵ J. H. Baxendale and D. Smithies, *Z. Phys. Chem. (Frankfurt)*, 1956, **14**, 323; J. H. Baxendale, R. S. Dixon, and D. A. Stott, *Trans. Faraday Soc.*, 1968, **64**, 2389.

different. For example, the reactivity ratio mesitylene:benzene would be doubled, since there are three positions in mesitylene but six in benzene. All the other compounds in the list are monosubstituted benzenes where the aromatic positions are not equivalent and, without knowledge of the relative reactivity of *ortho*-, *meta*-, and *para*-positions, it is not possible to evaluate reactivities per position. This problem is further considered in the following paper.

Table 19 also gives similar relative reactivities for the reaction of other reactive radicals, carbene, and nitrene species with these aromatic compounds, as taken from the literature, and values of $10^{-\sigma_p}$, *i.e.* relative reactivities based on σ_p parameters for a reaction with $\rho = 1$.

It is evident that most of these reactive species display a similar reactivity sequence to tritium, which corresponds to the expectation for mildly electrophilic reagents. In several of these cases it has been noted before that there is an approximate correlation with σ_p parameters. Methyl radicals (results not tabulated) form an exception and give an inverse order.³⁶ The best correlation with tritium atom reactivities is found for the trifluoromethyl radical and, surprisingly, for the photolytically generated ethoxycarbonylnitrene, for which the numerical values are in remarkably close agreement with our results. Despite qualitative trends, an interpretation in terms of polar effects alone does not appear promising. In a heterolytic electrophilic reaction (for which σ_p parameters are appropriate), as a reaction

³⁶ W. J. Heilman, A. Rembaum, and M. Szwarc, *J. Chem. Soc.*, 1957, 1127; *cf.* S. J. Hammond and G. H. Williams, *J.C.S. Perkin II*, 1973, 484.

of HeT^+ should be,³⁷ the attack of the reagent results in a dienyl system with a cationic charge and an even number of electrons. In the homolytic reactions, of which that of tritium atoms is typical, the product is a radical and the dienyl system contains an odd number of electrons. The effect of a substituent group is therefore, to some extent, expected to reflect its ability to stabilise the odd spin. It could therefore be a coincidence that ethoxycarbonylnitrene resembles the tritium atom in its selectivity, if this nitrene is indeed a singlet species³⁸ under the reaction conditions.

³⁷ F. Cacace, R. Cipollini, and G. Ciranna, *J. Chem. Soc. (B)*, 1971, 2089.

It would, however, be intelligible to find similar selectivities for tritium atoms and a *triplet* nitrene, and other evidence suggests that it may be the reaction of a triplet nitrene³⁹ to which the rate data quoted in Table 19 refer.

We thank the S.R.C. for financial support and Professors J. E. Baldwin and C. W. Rees for drawing our attention to refs. 38 and 39, respectively.

[3/297 Received, 9th February, 1973]

³⁸ J. E. Baldwin and R. A. Smith, *J. Amer. Chem. Soc.*, 1967, **89**, 1886.

³⁹ W. Lwowski and R. L. Johnson, *Tetrahedron Letters*, 1967, 891.
