Cyclohexyl *p*-Iodobenzoate.—Two grams of cyclohexanol and 6.00 g. of *p*-iodobenzoyl chloride were combined in 38 ml. of pyridine. After two hours at 0°, work up produced an oil which was dissolved in Skellysolve B and chromatographed on a Florisil column (60–100 mesh, 20 × 2.5 cm.). Eluates totalling 70 ml. produced 4.08 g. (62%) of a colorless oil which crystallized, after seeding, into beautiful fern-like crystals, m.p. 42–43°; recrystallized from methanol-water, m.p. 42–43°.

Anal. Calcd. for $C_{13}H_{15}O_2I$: C, 47.29; H, 4.58. Found: C, 47.38; H, 4.21.

Transesterification of Cyclocohexyl *p*-Iodobenzoate.—An anhydrous solution of 0.83 g. of cyclohexyl *p*-iodobenzoate and 0.08 g. of potassium cyanide in 25 ml. of methanol was refluxed for eight hours. Work up and subsequent crystallization from acetone–water gave 0.46 g. (70%) of the methyl ester,[7] m.p. 112–114°, undepressed upon mixture with an authentic sample of the ester. From the mother liquor was isolated 0.05 g. (8%) of *p*-iodobenzoic acid.

In another run the transesterification reaction was refluxed for only two hours, in which case the material originally isolated had m.p. 90–112° indicating that the transesterification was not complete after this time.

Cholesteryl *p*-Iodobenzoate.—A solution of 5.80 g. of cholesterol in 50 ml. of anhydrous pyridine was treated with 4.00 g. of *p*-iodobenzoyl chloride and 20 ml. of pyridine added to effect complete solution. The solution was heated to boiling and then permitted to cool to room temperature. Work up, followed by crystallization from benzene-methanol gave 6.72 g. (73%) of the ester as plates, m.p. 183–184° to a blue fluorescent, refractive melt which cleared at 205–225°, $\alpha^{28}D$ +2.4° (*c* 2.17).

(7) This methyl ester is easily recognizable, even in low concentrations, by its powerful anisole-like odor.

Anal. Calcd. for $C_{34}H_{49}O_2I$: C, 66.21; H, 8.01. Found: C, 66.36; H, 8.01.

Transesterification of Cholesteryl *p*-Iodobenzoate in Methanol.—A sample of 2.82 g. of cholesteryl *p*-iodobenzoate was dissolved in 200 ml. of hot benzene. To this solution was added 1.5 g. of potassium cyanide in 200 ml. of methanol. After 7.5 hours of reflux, 200 ml. of liquid was distilled from the reaction mixture. This distillate, upon evaporation, left 0.82 g. of unchanged starting material. The 200 ml. of solution remaining was evaporated to a solid residue which was extracted with ether. The ether extract was evaporated and the resulting solid chromatographed in benzene on a Florisil column (60–100 mesh, 20 × 2.5 cm.). From the first two 150-ml. fractions there was recovered 0.55 g. (65% based on all cholesteryl *p*-iodobenzoate not actually recovered) of methyl *p*-iodobenzoate, m.p. 109–112°. After an additional 250 ml. of benzene had passed, a solid, m.p. 146–148°, was recovered from the eluate and the column was flushed with acetone; 0.95 g. (68% calculated as above) of cholesterol, m.p. 146°, was thus produced.

In another run all reagents and solvents were carefully dried before use and the reflux continued for 18 hours. Chromatography on alumina produced a quantitative yield of cholesterol and an 85% yield of methyl *p*-iodobenzoate.

Transesterification of Cholesteryl *p*-Iodobenzoate in Cyclohexanol.—One gram of cholesteryl *p*-iodobenzoate was dissolved in 200 ml. of refluxing cyclohexanol and 0.5 g. of potassium cyanide was added. After six hours of reflux the mixture was evaporated to dryness. The residue, when chromatographed in benzene on a 20 cm. × 2.5 cm., 60–100 mesh Florisil column gave 0.29 g. (54%) of cyclohexyl *p*-iodobenzoate, m.p. 40–41°, in the first 140 ml. of eluate. Acetone removed 0.52 g. (80%) of cholesterol, m.p. 145–147°, from the column.

MIDDLETOWN, CONNECTICUT

The Mechanisms of Diazonium Salt Reactions. I. The Products of the Reactions of Benzenediazonium Salts with Methanol

BY DELOS F. DETAR[1] AND MELVIN N. TURETZKY[2]

Quantitative product studies of the thermal decomposition of benzenediazonium chloride or fluoborate in methanol have shown that anisole (93%) is the principal organic product under acidic conditions; this result points to a heterolytic cleavage of the diazonium C–N bond in the presence of acid. With acetate buffers the reaction is much more complex. Some anisole is produced, but the main product is benzene; smaller amounts of biphenyl and traces of azobenzene also are formed. Oxygen has a most pronounced effect on the reaction; in the presence of oxygen the product mixture is dark brown, and the above products account for only 30–75% of the diazonium salt used. In the absence of oxygen (vacuum train techniques) the reaction is much faster, the product mixture is almost colorless, and 98% or more of the diazonium salt can be accounted for. The reaction in the presence of acetate buffers is almost certainly a free radical chain process, and a new type of electron transfer reaction $\cdot CH_2OH + C_6H_5N_2{}^+ \rightarrow CH_2OH^{\oplus} + C_6H_5\cdot + N_2$ has been proposed as an essential step. It has been possible to exclude the radical addition step $C_6H_5\cdot + C_6H_6 \rightarrow C_6H_5C_6H_5 + H\cdot$ as a source of biphenyl in these reactions since the yield of biphenyl is not increased by addition of benzene to the reaction mixture. A tentative over-all mechanism is summarized in eq. 1–8. In an incidental investigation it was found that solutions of azobenzene in methanol on exposure to daylight or to a tungsten light in glass flasks give an equilibrium mixture of *cis*-azobenzene and *trans*-azobenzene containing 27–28% of the *cis* isomer.

One of the serious difficulties in interpreting the reactions of free radical intermediates is the lack of information about important details of the mechanisms of these complex reactions. These difficulties have been emphasized by Bartlett and Nozaki[3] and by Edwards and Mayo[4] for the reactions of diacyl peroxides. Under certain conditions as, for example, in the Gomberg–Bachmann reaction[5] di-

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(2) Rohm and Haas Research Assistant 1950–1951; U. S. Rubber Research Fellow 1952–1953 at Cornell University.

(3) P. D. Bartlett and K. Nozaki, THIS JOURNAL, 69, 2299 (1947).

(4) F. G. Edwards and F. R. Mayo, *ibid.*, 72, 1265 (1950).

(5) W. E. Bachmann and R. A. Hoffman, "Organic Reactions," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 224.

azonium salts constitute useful sources of free radical intermediates. We have undertaken a study of the mechanisms of the cleavage of the C–N bond of diazonium salts with the hope that such studies will lead to a greater understanding of a number of free radical reactions and also to a better understanding of the reactions of the versatile diazonium salts themselves.[6]

It has been known for some time that the C–N bond of diazonium salts can undergo cleavage by at least two distinct processes,[6d] a heterolytic process

(6) (a) D. F. DeTar and H. J. Scheifele, Jr., THIS JOURNAL, 73, 1442 (1951); (b) D. F. DeTar and D. I. Relyea, *ibid.*, 76, 1680 (1954); (c) D. F. DeTar and Y. W. Chu, *ibid.*, 76, 1686 (1954); (d) D. F. DeTar and S. V. Sagmanli, *ibid.*, 72, 965 (1950).

PRODUCTS OF THE REACTION OF BENZENEDIAZONIUM CHLORIDE AND BENZENEDIAZONIUM FLUOBORATE WITH METHANOL

Run	CH_3-OH, ml.	C_6H_5-N_2X^a	Reactants, mmoles Na-OAc	HOAc	C_5H_5	O_2	N_2, %	$C_6H_5OCH_3$	Products, mmoles, % C_6H_5	Biphenyl	Azobenzene	Other
1	50	4.94				Yes[b]	[c]	4.69 ± 0.13(95%)	0.5 ± 0.3	<0.005	0	[d]
2	50	4.94				Yes		4.60(93%)	.3	< .005	0	[d]
3	40	0.750				Yes		0.687(92)	.03	< .004	0	[d]
4	50	5.00	11.0			Yes	[e]	.15(3)	2.88(58)	0.28(11)	0.03(1)	
5	50	5.00	11.0			Yes		.12(2.5)	3.00(60)	.30(12)	.04(1.5)	
6	25	4.96	11.0			Yes		.25(5)	2.5(50)	.42(17)	.02(1)	
7	15	4.98	11.0			Yes		.36(7)	1.6(32)	.45(18)	.03(1)	
8	80	1.33	2.3			Yes		.07(5)	0.30(23)	.02(3)	.01(1)	
9	75	0.96	2.2			Yes		.07(7)	0.19(20)	.007(2)	.003(1)	
10	50	4.59	11.0		11.2	Yes		.36(7)	14.30(67)[f]	.33(14)	.04(1.5)	
236	50	0.928	9.5	22.4		No[g]	98.7	.055(6)[m]	0.810(87)[m]	.0207(4.5)[m]	.00314(0.68)[m]	(6.5)[l,n]
238	50	.926	9.5	22.4		No[h]	96.0	.032(3.5)	.809(87)	.0214(4.5)	.00276(0.6)	(3.7)[n]
240	50	.927	9.5	22.4		1%[i]	80.1[j]	.127(14)	.56(60)	.0144(3)	.00564(1.2)	(14.2)[n]
210	50	.931[k]	9.5	22.4		No	100.3	.016(1.7)	.86(92)	.0206(4.4)	.0027(0.58)	(2.1)[n]
242	50	.936	9.5	22.4	1.87	No	98.3	.029(3.1)	2.57(75)[f]	.0230(4.9)	.00265(0.57)	(3.1)[n]
243	50	.947	9.5	22.4	3.94	No	98.8	.037(3.9)	4.68(78)[f]	.0237(5)	.0030(0.6)	(4.2)[n]

[a] Runs 1–10 benzenediazonium chloride carried out at room temperature (about 25°); 236, etc., benzenediazonium fluoborate kinetic runs carried out at 15°. [b] Runs in 1–10 carried out in presence of air. [c] Under acidic conditions the yield of nitrogen was found to be quantitative; some of the diazonium salt samples were assayed by measurement of nitrogen evolved and showed consistent 97–100% purity. [d] Chlorobenzene may well have been present, but amount was below limits of positive identification by ultraviolet spectrophotometric means in presence of the stated amount of anisole (<10% yield). [e] Apparent amount of N_2 evolved ranged from 40–60% in similar runs; see text. [f] % yield based on difference between benzene taken and benzene found; it is liable to an error of at least 2% of the total amount of benzene present. [g] Outgassed in vacuum train; see Experimental. [h] Different outgassed methanol sample. [i] Gas admitted to free space (470 cc.) in flask contained about 1% oxygen; 0.2 mmole of oxygen was thus present. [j] Allowance not made for amount of oxygen used up since no estimate was available. [k] 1.96 mg. of anhydrous copper sulfate was present. [l] Formaldehyde, benzyl alcohol and phenyl acetate were shown to be present; see Experimental section. [m] Standard deviations are about 2% relative for benzene and 5% relative for the other compounds. [n] Anisole yields expected on the hypothesis that the anisole is produced entirely by the ionic reaction (eq. 8).

(probably of the SN1 type) under acidic conditions, and a homolytic process under other conditions as in the presence of alkali (Gomberg–Bachmann reaction) or in the presence of reducing agents as in the hypophosphite reduction.[7]

A study of the reactions of diazonium salts in alcohols has been undertaken since it has been found possible to emphasize either the heterolytic processes or the homolytic processes under suitable conditions and because the use of this homogeneous reaction medium makes feasible the study of the mechanisms by use of both reaction kinetic studies and product studies. The present work is concerned with a study of the products of the thermal decomposition of benzenediazonium chloride and fluoborate in methanol at various levels of acidity.

Previous workers[8–10] have reported that benzenediazonium salts react with methanol to give anisole under acidic conditions. In the presence of sodium carbonate or of sodium hydroxide, Beeson[9] obtained varying yields of benzene and biphenyl along with unidentified highly colored products.

We have undertaken a more comprehensive quantitative study of the reaction products using a spectrophotometric analytical technique for most of the products. The results are summarized in Table I.

In the absence of buffers the reaction mixture becomes acidic as the diazonium salt decomposes. Runs 1–3 are typical; anisole is the major product (93%). The absence of azobenzene is shown qualitatively by the fact that the reaction mixture is colorless. The yield of biphenyl is less than 1%, pos-

(7) N. Kornblum, G. D. Cooper and J. E. Taylor, This Journal, 72, 3013 (1950).

(8) A. Hantzsch and E. Jochem, Ber., 34, 3337 (1901).

(9) J. L. Beeson, Am. Chem. J., 16, 235 (1894), detailed report of many preparative runs.

(10) A. W. Hofmann, Ber., 17, 1917 (1884).

sibly very much less. Some benzene is barely detectable by the presence of the typical absorbance peaks and valleys, but it is difficult to analyze accurately for small amounts of weakly absorbing benzene in the presence of large amounts of strongly absorbing anisole. Since anisole is the product expected for the heterolytic SN replacement of the diazonium nitrogen, and since kinetic evidence shows that the closely related thermal decomposition of benzenediazonium salts in water is a heterolytic SN process,[6b,d] it seems safe to conclude that a heterolytic cleavage of the C–N diazonium salt bond is involved in these reactions (eq. 8).

In the presence of sodium acetate or of an acetate buffer the reaction is entirely different. As normally run the reaction mixture is dark brown in color and the principal volatile product is benzene. Some anisole is present along with a little biphenyl and azobenzene. These products account for about 70% or less of the diazonium salt. Attempts to obtain other products by chromatographic techniques yielded small amounts of a number of other substances which did not seem worth further investigation at the time.

On the basis of the pronounced effect of oxygen on the reaction rates, a series of product studies was carried out on acetate-buffered reactions in the absence of oxygen insofar as this is attainable by vacuum train techniques.[11] These reaction mixtures (236–238, 210–243 inclusive) were very faintly yellow in color, and about 97% of the diazonium salt could be accounted for. Benzene (85–90%) was the principal product under the oxygen free conditions, some anisole and biphenyl (4.5%) accounted for another 7–11%. The yield of azobenzene was fairly constant at 0.6%. The reduction of the diazonium ion to benzene and to biphenyl was coupled
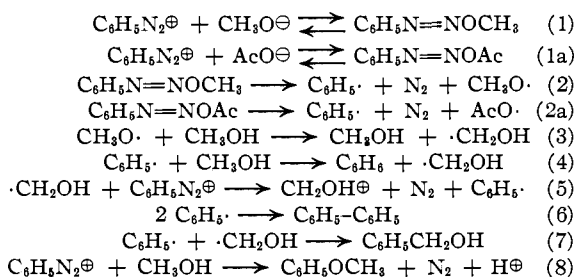
(11) D. F. DeTar and M. N. Turetzky, in preparation.

with oxidation of the methanol to formaldehyde. Formaldehyde was determined gravimetrically as the methone derivative for several runs not recorded in Table I, and yields of 80, 100, 90, 80 and 84% were obtained. It appears that some 80–90 mole % of formaldehyde is formed per mole of diazonium salt decomposed. Since anisole yields in these runs were probably of the order of 10% (judging from the over-all rate of these reactions as compared with the last six in Table I), these figures admit the possibility of the formaldehyde yield being equivalent to the yield of reduction products. Two further reaction products were detected in small amounts by a semi-quantitative infrared method. These were benzyl alcohol (about 1% and phenyl acetate (about 0.5%).

Nitrogen yields were obtained incidentally in the course of the kinetic runs.[11] With a precision of about 1.5% the nitrogen yields under acidic conditions and in the outgassed solutions were 98.5%. In the presence of air the apparent nitrogen yields ranged from about 40–60%. Analysis of residues showed that some nitrogen was present, though not as much as the 40–60% deficit required. But since the nitrogen yields are based on a differential manometric method, it is not possible to distinguish between a nitrogen deficit of 1 millimole on the one hand and an oxygen absorption of 0.5 millimole on the other. The absorption of oxygen might well lead to the formation of highly colored quinonoid products. The available data do not permit an estimate of either the actual nitrogen yield nor of the amount of oxygen absorbed beyond the limits indicated. At one point in the work it was considered that the nitrogen deficit might be due to the formation of an isodiazotate or other stabilized diazonium salt derivative. In several experiments the reaction mixture was acidified and reconnected to the manometer system, but there was no evidence of any further reaction.

Discussion

The products of the thermal decomposition of benzenediazonium salts in methanol containing an acetate buffer are largely those expected of a reaction that involves a homolytic cleavage of the C–N bond. The pronounced inhibitory effect of oxygen, discussed in more detail in another paper,[11] suggests that a chain reaction is involved. The problem is to discover mechanisms that will give the products and to try to devise suitable tests to distinguish among alternative mechanisms. A proposed mechanism is given in equations 1–8.

$$C_6H_5N_2^\oplus + CH_3O^\ominus \rightleftarrows C_6H_5N{=}NOCH_3 \quad (1)$$

$$C_6H_5N_2^\oplus + AcO^\ominus \rightleftarrows C_6H_5N{=}NOAc \quad (1a)$$

$$C_6H_5N{=}NOCH_3 \longrightarrow C_6H_5\cdot + N_2 + CH_3O\cdot \quad (2)$$

$$C_6H_5N{=}NOAc \longrightarrow C_6H_5\cdot + N_2 + AcO\cdot \quad (2a)$$

$$CH_3O\cdot + CH_3OH \longrightarrow CH_3OH + \cdot CH_2OH \quad (3)$$

$$C_6H_5\cdot + CH_3OH \longrightarrow C_6H_6 + \cdot CH_2OH \quad (4)$$

$$\cdot CH_2OH + C_6H_5N_2^\oplus \longrightarrow CH_2OH^\oplus + N_2 + C_6H_5\cdot \quad (5)$$

$$2\ C_6H_5\cdot \longrightarrow C_6H_5{-}C_6H_5 \quad (6)$$

$$C_6H_5\cdot + \cdot CH_2OH \longrightarrow C_6H_5CH_2OH \quad (7)$$

$$C_6H_5N_2^\oplus + CH_3OH \longrightarrow C_6H_5OCH_3 + N_2 + H^\oplus \quad (8)$$

The anisole might be produced by the ionic reaction (eq. 8) or it might be due to some other reaction such as the combination of a phenyl radical with a methoxyl radical. Since the rate of the ionic decomposition of diazonium salts in water is insensitive to the anion present, it is reasonable to assume that the rate of anisole formation by the ionic process is also relatively insensitive to the presence of the acetate buffer. This rate is given by eq. 9.
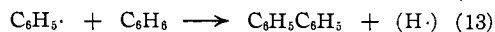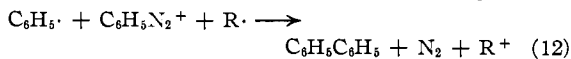
$$d[\text{anisole}]/dt = k'_8[C_6H_5N_2^\oplus] \quad (9)$$

$$d(\%\ \text{anisole})/dt = 93k_8[C_6H_5N_2^\oplus]/[C_6H_5N_2^\oplus]_0 \quad (10)$$

In eq. 9 the rate constant k_8' is equal to 0.93 k_8 where k_8 is the rate of nitrogen evolution. The coefficient 0.93 allows for the 93% anisole yield as reported in Table I. The rate constant k_8 is 1.13×10^{-3} min.$^{-1}$ as calculated from data reported by Pray[12] using the expression $\ln k = 41.0335 - 27.3661RT$, which fits his values for 20, 30 and 40° and our values at 25° with a standard deviation of about 0.5% in k. Although the over-all reactions are too complex to be described by a simple function, expected anisole yields can be calculated by graphical integration of eq. 11. The required percentage reaction–time plot is made by plotting $100(p_\infty - p)/$

$$\%\ \text{anisole} = 0.93\ k_8 \int_0^\infty (\%\ \text{reaction})dt \quad (11)$$

$(p_\infty - p_0)$ against time. The calculated anisole yields are given in Table I in the column headed "Other Products." It is clear that all of the anisole can be attributed to the ionic reaction and that little, if any, can be due to other reactions. The trace of phenyl acetate produced would also be a by-product of the ionic reaction. Although radical combination reactions between phenyl radicals and methoxyl radicals or acetoxyl radicals are not entirely excluded, they may at least be relegated to the background until positive evidence requires their reconsideration.

There are three types of reaction that might lead to biphenyl formation. These types are illustrated in eq. 6, 12 and 13. Equation 6 is self-explanatory,

$$C_6H_5\cdot + C_6H_5N_2^+ + R\cdot \longrightarrow$$
$$C_6H_5C_6H_5 + N_2 + R^+ \quad (12)$$

$$C_6H_5\cdot + C_6H_6 \longrightarrow C_6H_5C_6H_5 + (H\cdot) \quad (13)$$

and so is eq. 13 except for the fact that the reaction may involve two stages and another radical in order that a free hydrogen atom need not be involved. Equation 12 is intended to represent the various reactions in which a phenyl radical can combine with a diazonium salt or a covalent diazo compound. These reactions summarize all of the simple processes that can lead to biphenyl production.

A relatively simple test can be applied to distinguish the radical addition process (eq. 13) from the other two. The addition of benzene should greatly increase the yield of biphenyl if radical addition is the source. A comparison of runs 4 and 5 with 10 and of runs 236 and 238 with 242 and 243 (Table I) shows that added benzene has little or no effect on the yield of biphenyl. This result permits the definite exclusion of the radical addition step (eq. 13) for these reaction conditions.

Possibilities for the free radical chain reactions leading to benzene are given in eq. 4 and 5 and eq.

(12) H. A. Pray. J. Phys. Chem., 30, 1417, 1477 (1926).

4 and 14. The abstraction of a hydrogen atom from the methanol carbon atom to give a hydroxymethyl radical rather than from the oxygen to

$$\cdot CH_2OH + C_6H_5N_2OCH_3 \longrightarrow$$
$$C_6H_5\cdot + N_2 + CH_3OCH_2OH \quad (14)$$
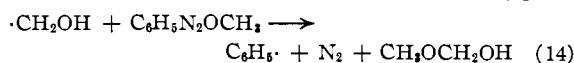
give a methoxyl radical was indicated by Urry.[13] Equation 14 involves the reaction of a free radical intermediate with a covalent diazo compound such as the diazo methyl ether. Since this step requires a reasonably high concentration of the diazo ether for plausibility, information about the formation equilibria for these covalent diazo compounds is relevant. In aqueous solution, equilibria of the type shown in eq. 15 are definitely in favor of the diazonium ion. An attempt was made to extract ben-

$$C_6H_5N_2^{\oplus} + AcO^{\ominus} \rightleftharpoons C_6H_5N_2OAc \quad (15)$$
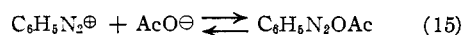
zenediazoacetate with toluene from concentrated aqueous solutions containing benzenediazonium ions and acetate ions. Under a variety of conditions the amount of diazo compound extracted into the organic layer was negligible. Since the formation of the diazoacetate would be further enhanced by a favorable distribution constant, the covalent compound being more soluble in toluene than in water, the absence of detectable diazo compound in the toluene layer indicates that the equilibrium constant of eq. 15 must be very small; it is estimated to be less than 10^{-5} mole^{-1} l., perhaps much less. Lewis[14] has reported that the ultraviolet spectra of several diazonium salt solutions are little affected by the addition of acetate ion, further evidence for a small equilibrium constant.

Although equilibria have not been investigated in methanolic solution, it seems reasonable to suppose that a reaction requiring a covalent diazo compound (eq. 14) cannot be an essential step of a rapid chain process. Thus for $[C_6H_5N_2OAc]/[C_6H_5N_2^+]$ to be as large as 10^{-2}, K_{1a} would have to be almost 10^{-1} or K_1 would have to be much larger than 10^6.

The reaction of a hydroxymethyl radical with a diazonium cation (eq. 5) represents an alternative chain-carrying step; this step is an electron transfer reaction. Examples of electron transfer reactions between two organic molecules are rare although electron transfer reactions with metallic ions are fairly common. Kornblum[7] has suggested an electron transfer reaction (eq. 16) or some variant

$$C_6H_5N_2^{\oplus} + \cdot HPO_2^{\ominus} \longrightarrow C_6H_5\cdot + N_2 + HPO_2 \quad (16)$$
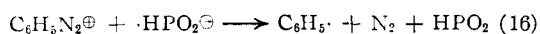
as a part of a chain mechanism for the reduction of diazonium salts with hypophosphorus acid. Equation 5 is a plausible electron transfer reaction since the hydroxymethyl radical is converted to a relatively stable molecule, viz., protonated formaldehyde.

Although the concentration of covalent diazo compounds is probably low, the initiation step would seem to require as intermediates, eq. 2 or eq. 2a. These reactions have been postulated frequently as sources of free radicals from diazonium compounds.

Possible termination steps are given in eq. 6, 7

and 12. The presence of a little benzyl alcohol is perhaps explained by eq. 7, though other steps leading to this product can be formulated. The explanation of the azobenzene formation might be a radical combination reaction, eq. 17, but such an

$$C_6H_5N_2\cdot + C_6H_5\cdot \longrightarrow C_6H_5N=NC_6H_5 \quad (17)$$
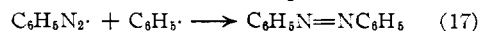
explanation poses certain problems. This reaction requires a fairly high concentration of phenylazo radicals and this implies a considerably lower reactivity (longer life) of these radicals than of the phenyl radicals which are regenerated by the chain process. Perhaps the most obvious alternate source of azobenzene is eq. 12 written to give azobenzene instead of biphenyl.

On the basis of the product studies, therefore, a plausible chain mechanism has been built up for the thermal decomposition of benzenediazonium salts in oxygen-free methanol in the presence of an acetic acid–sodium acetate buffer. This mechanism is summarized in eq. 1–8. The pronounced effect of oxygen on the reaction is accounted for by reaction of phenyl radicals or hydroxymethyl radicals with oxygen to form peroxy radicals which exert an oxidizing effect either directly or indirectly through reaction of hydroperoxide intermediates.

Experimental Part

Preparation of Reference Compounds.—The reference compounds were reagent grade materials which were carefully repurified. Although m.p. and refractive index measurements provided evidence of purity, the criterion adopted was constancy of extinction coefficients for the samples on continued purification.

Biphenyl was recrystallized from ethanol, m.p. 69.1–69.9° cor. Reagent grade benzene was fractionally frozen. Anisole was refluxed with sodium methoxide to destroy any unchanged methyl sulfate.[15] It was then put through a column of alumina and finally distilled under reduced pressure; it has $n^{20}D$ 1.5169.

cis-Azobenzene, *trans*-Azobenzene and Their Photoequilibration.—*trans*-Azobenzene was purified by chromatography on F-20 alumina[16] using a benzene–heptane mixture (1:4) as solvent. It then was recrystallized from ethanol. A 10-g. sample of the above purified *trans*-azobenzene was dissolved in 40 ml. of 4:1 *n*-heptane–benzene. The solution was exposed to daylight for four days (four hours would probably suffice) and then a 10-ml. aliquot was placed on a 12 × 1.5 cm. column of Brockmann[6b,17] Grade 2 alumina and developed with an additional 40 ml. of the heptane–benzene solvent. The *trans*-azobenzene was thereby washed from the column, and the upper diffuse band of *cis*-azobenzene was eluted with 40 ml. of anhydrous ether, giving 0.18 g. of *cis*-azobenzene. Grade 3 alumina worked about as well. The samples were rechromatographed for further purification. The purity of the *cis*- and *trans*-azobenzene was established by the infrared spectra. Mineral oil mulls of the *trans* compound had peaks at 8.18, 8.67 and at 9.78 μ which were absent in the *cis* compound, and *cis*-azobenzene has a strong peak at 13.14 μ which is absent in the *trans* compound.

In obtaining extinction coefficients of *cis*-azobenzene in the ultraviolet region, the solutions were prepared in diffuse light and were kept in the dark until readings could be obtained. The readings were completed within one to two hours after the solutions had been prepared. It was demonstrated that half-hour exposure to the full (2 mm.) beam of the spectrophotometer at 2560, 2640, 2750 or at 3100 Å. caused no detectable equilibration. This was true in spite of the fact that the spectrophotometer was equipped with a Nester hydrogen lamp which is more intense than the Beckman lamp.

(13) W. H. Urry, F. W. Stacey, E. S. Huyser and O. O. Juveland, This Journal, **76**, 450 (1954).

(14) E. S. Lewis, private communication.

(15) L. I. Smith, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 361.

(16) Aluminum Ore Co. Chromatographic grade alumina

(17) H. Brockmann and H. Schodder, Ber., **74**, 73 (1941)

On exposure to bright daylight or to a tungsten lamp for three hours or more in glass flasks, the methanolic solutions came to equilibrium. Four equilibrations were made from the *cis* and four from the *trans* side. A variance analysis was carried out on two blocks each of 44 extinction coefficients at 11 wave lengths (2430–2775 inclusive), one block involving equilibria from the *cis* side, the other involving equilibria from the *trans* side. The among wave lengths variance was eliminated and the between blocks variance (0.000846) on comparison with the residual variance (0.001286) showed that there was no significant difference between the two blocks of extinction coefficients, and that equilibrium had in fact been attained. The variance analysis was carried out on the natural logarithms of the extinction coefficients. The equilibrium solution (methanol) contains 27.5 ± 0.5% of *cis*-azobenzene.

Reactions and Product Isolation.—The reactions were carried out in distilling flasks or in 500-ml. ground joint flasks. The oxygen-free reaction mixtures were prepared on a vacuum train as described elsewhere[11] and represent runs for which kinetic data also were obtained.

Products were isolated by distillation using a one piece specially constructed head containing a sealed in dropping funnel and a condenser. The first fraction, containing most of the benzene, was collected separately. A second fraction was obtained by distilling the methanol to dryness, submerging the flask in an oil-bath maintained at 140–150°, and then dropping 100 ml. of methanol gradually onto the hot residue. In this fashion the small amounts of biphenyl and azobenzene were quantitatively swept over into the receiver. The receivers used were volumetric flasks and the solutions were diluted appropriately for analysis.

In one experiment 8 mmoles of benzenediazonium fluoborate was allowed to decompose in 250 ml. of outgassed methanol in the presence of an acetate buffer. After completion of the reaction (about an hour) sodium methoxide was added to neutralize the excess acetic acid present. The methanol was stripped through a column until only 10 ml. remained, this was filtered and the solid sodium acetate and the methanol layer were extracted with three 25-ml. portions of carbon tetrachloride (the sodium acetate renders the methanol insoluble in carbon tetrachloride). Distillation of the carbon tetrachloride removed the rest of the methanol. The carbon tetrachloride solution was concentrated to less than 1 ml., transferred to a 0.2-mm. fixed cell, and the infrared spectral curve run on a Perkin–Elmer model 21 spectrophotometer against a matched cell containing solvent only. Three samples of known constitution were put through the distillation and spectral procedure. Each of these known samples contained anisole, biphenyl and azobenzene; one sample contained in addition 1% of benzyl alcohol and the other contained in addition 1% of phenyl acetate. The peaks observed in the unknown carbon tetrachloride solution could all be accounted for in terms of these five compounds, and in addition a rough estimate of the yields could be made.

Ultraviolet Spectrophotometric Analyses.—Spectra were obtained on a Beckman model DU spectrophotometer. Since four compounds were to be determined routinely, absorbance values at a minimum of four wave lengths were needed. But since there was no *a priori* way of knowing that additional products were definitely absent, a total of twelve wave lengths was used, and the observed absorbances were carefully compared with absorbances calculated for the amounts of anisole, azobenzene, benzene and biphenyl found for evidence of interference. For the runs in the absence of oxygen and for the acidic runs interference was absent, but the runs made in the presence of air contained small amounts of unidentified colored material absorbing more strongly at 3600 than at 3100 Å. (in contrast to azobenzene). This interference reduces the accuracy of those runs somewhat.

To increase accuracy and to help to avoid errors, the absorbance values were determined in duplicate, first with solvent in cell one and solution in cell two, and then with the cells reversed. It is easily shown that the average of these two absorbance values gives an absorbance which is free of any difference in absorbance of the cells, and one for which the light path length is the average of the path length in the two cells. Absorbance values were kept between 0.2 and 0.8 insofar as possible since this region is the one of maximum sensitivity and accuracy.

The absorptivities obtained on the reference compounds

are given in Table II. Those required for the analyses were obtained independently in quadruplicate.

TABLE II

MOLAR ABSORPTIVITIES[a] (EXTINCTION COEFFICIENTS) IN METHANOL

λ, Å.	Benzene[b,e]	Anisole[b,f]	Biphenyl[b]	Azobenzene,[g] equil.	cis-azobenzene[c]	trans-azobenzene[c]	Phenyl acetate[d]
2430	95.4	115.6	16,460	5040	9960	3120	127
2460	54.6	170.3	17,210	4540	9660	2540	139
2485	157.8	237.2	17,260	4250	9140	2330	154
2520	60.7	361.1	16,450	3850	7790	2280	191
2545	193.4	485.7	15,320	3600	6560	2370	211
2585	48.0	753	12,760	3400	4950	2690	252
2605	131.8	899	11,280	3450	4470	2940	249
2640	28.7	12,510	8,860	3770	4160	3470	224
2710	1.9	17,520	4,640	5030	4550	5080	126
2750		12,200	2,850	5970	4800	6360	87
2775		14,410	1,985	6670	4920	7210	76
2950		(<100)	(<100)	12,370	4530	15,190	
3000				14,020	4084	17,640	
3100				16,360	3040	21,220	

[a] $\epsilon = a/bc$; a = absorbance (optical density), b = cell length (1.000 cm.), c = concn. in moles per liter. Individual values of ϵ have a standard deviation of 1.5% relative. Slit width 0.5 mm. nominal at all wave lengths. Omitted values were negligible. [b] Std. dev. of avg. of four, 0.8% relative. [c] Std. dev. of avg. of two, 1.1% rel. [d] Std. dev. about 2%. [e] All points represent maxima and minima except 2640 and 2710. [f] 2710 and 2775 are maxima, 2750 is a minimum. [g] Approached from both the *cis*- and from the *trans*-azobenzene side by illuminating solutions with incandescent bulb or with daylight in glass flask; contains 27.5 ± 0.5% of *cis*-azobenzene. Std. dev. of avg. of eight, 1.3% relative.

The procedure for analyzing the solutions obtained as distillates (appropriately diluted and equilibrated in light) was as follows: If azobenzene was present, its concentration was determined from the absorbance at 2950, 3000 and 3100; the absorbances were added and divided by the total of the absorptivities of equilibrated azobenzene. The remaining absorbance values were corrected by subtracting out the azobenzene contribution.

Although least squares methods have been applied to the determinations, the procedure is a lengthy one, and an averaging method was found to work out satisfactorily. Averages of the absorbances of the solutions and averages of the absorptivities of anisole, benzene and biphenyl were obtained at three sets of wave lengths; 2430, 2485 and 2545 (representing benzene maxima); 2460 and 2520 (benzene minima); 2710 and 2775 (anisole maxima). The resulting three equations in three unknowns were solved using the reciprocal matrix values.

Finally absorbances were calculated for each wave length for a solution of the composition found. In some cases it was observed that sufficient acetic acid was present to cause discrepancies at 2430, 2460, 2485 and 2520. This was corrected empirically using the respective absorptivities 13.4, 7.09, 3.84 and 1.56. The concentration calculation then was repeated. The final concentrations gave a standard deviation of the absorbance of 0.005, a value which compares closely with the value calculated from the standardization runs.

The analyses of eight known solutions are presented in Table III. The necessity of using two distillate fractions per determination in order to improve benzene accuracy resulted in some loss of precision for the other components, but the over-all results are quite satisfactory.

Phenyl Acetate Determination.—The determination of a few mole per cent. of phenyl acetate in the presence of benzene, biphenyl, azobenzene, anisole, formaldehyde and methanol poses a difficult problem. The extinction coefficients (Table II) at all wave lengths are so low that a 5 mole per cent. quantity of phenyl acetate would lead to an absorbance of not more than 0.020 in the solutions actually measured under the very maximum conditions, and the most likely values would run about 0.005, values which are too low to detect as phenyl acetate since there is only the single broad maximum. A considerable amount of ex-

Table III

SPECTROPHOTOMETRIC ANALYSIS OF KNOWN SOLUTIONS[a]

All entries are in mmoles except for the columns labeled % recovery

Buffer		Benzene		Recov., %	Biphenyl		Recov., %	Anisole		Recov., %	Azobenzene		Recov. %
NaOAc	HOAc	Taken	Found		Taken	Found		Taken	Found		Taken	Found	
		3.24	3.40	102	0.014	0.013	94	1.39	1.46	105			
		6.49	6.02	93	.015	.016	105	2.16	2.23	103			
		5.10	4.96	97	.0046	.0055		2.91	2.79	96			
		15.45	15.11	98	.0053	.0078		6.39	6.60	103			
9.5	44.2	2.06	1.99	97	.022	.022	100	.019	.019	100	0.0030	0.0027	91
0	0	.98	.97	99	.075	.074	99	.019	.020	105	.0030	.0027	91
0	0	1.93	2.02	104	.047	.048	102	....	....	..	....	....	..
9.5	44.2	.74	.75	101	1.018	1.004	99	.0096	.0085	89	.0022	.0021	92

[a] The first four solutions were made up in methanol and analyzed without further treatment. The last four solutions (with entries in the buffer columns) were put through the complete isolation procedure.

ploratory work was devoted to a titration method involving hydrolysis to phenol, bromination with a bromide–bromate mixture, and titration of excess bromine by treatment with potassium iodide, and titration with thiosulfate. This procedure was satisfactory on aqueous solutions, but methanol and the products interfered so that reproducible blanks were difficult to obtain. A 0.01-mmole sample of phenyl acetate could be determined with an accuracy of about ±0.01 mmole in the presence of 0.02 mmole of anisole and 0.005 mmole of azobenzene, and since 0.01 mmole represents rather more than the maximum expected yield, the titration method had insufficient sensitivity. The carbon tetrachloride extraction method described above seems to be the most promising method for determining phenyl acetate.

Formaldehyde Determination.—The absorption of formaldehyde solutions in methanol is low, due to the fact that the formaldehyde is largely present as the hemiacetal. The gravimetric determination of formaldehyde as the methone (5,5-dimethylcyclohexane-1,3-dione) derivative proved reasonably satisfactory on formalin samples. To 5 ml. of a methanol solution containing from 0.5 to 8 mg. of formaldehyde were added 5 ml. of water and 10 ml. of a saturated aqueous solution of methone. The solutions were allowed to stand for about 40 hours before filtration, and the precipitate was dried at 60°.

Attempts to Prepare a Toluene Solution of Benzenediazoacetate.—An aqueous solution of benzenediazonium chloride was prepared from 170 ml. of aniline, 380 ml. of concd. hydrochloric acid, 40 ml. of water and 250 ml. of sodium nitrite solution. Two five-ml. aliquots were run into 25 ml. of a stock solution of β-naphthol in 95% ethanol (10% solution) and 50 ml. of water. The resulting benzeneazo-β-naphthol weighed 2.41 g. and 2.45 g. indicating a molarity of 1.95. A solution of 110 g. of sodium acetate trihydrate in water was made up to a volume of 200 ml. This was cooled to 0° and 200 ml. of the diazonium stock solution was added. The titer of this diazonium acetate stock solution changed only slowly at 0° (initial, 0.96 M; after 90 min., 0.92, 0.92 M; after 210 min., 0.91 M; after 420 min., 0.86 M) as determined by weight of the β-naphthol-coupling product.

After ten minutes a 100-ml. portion of the diazonium acetate stock solution was extracted with 100 ml. of toluene at 0°. The aqueous layer was analyzed as above; 0.93, 1.02 M. The toluene layer was dried briefly over magnesium sulfate, then 50 ml. was added to 0.287 g. of β-naphthol in 50 ml. of ethanol, and 25 ml. was evaporated as a blank. The blank on evaporation gave a 42-mg. residue, the β-naphthol beaker on evaporation gave 75-mg. differential residue. The residue seemed to be hydroxyazobenzene which was found to be present in the stock solution. There was no characteristic benzeneazo-β-naphthol color. There is reason to believe that coupling will take place under the conditions used, for Huisgen[18] obtained quantitative yields of the coupling product in methanolic solutions.

Several of these extraction experiments were carried out with similar negative results. At higher pH levels (phosphate buffer, pH 6) decomposition was more rapid. More material was extracted into the toluene layer, but little, if any, coupling product was formed.

Assuming that the error in determination of the benzeneazo-β-naphthol is 25 mg., and further assuming that the distribution coefficient of the covalent diazoacetate is as low as 100 (in favor of the toluene), then the amount of covalent acetate in the aqueous solution would be a maximum of 0.002 mmole, and the equilibrium constant for equation 15 would be less than 10^{-5} mole^{-1} l.

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(18) R. Huisgen and G. Horeld. *Ann.*, **562**, 137 (1949).