Ethers and Ketones.—4,4′-Diaminodiphenyl ether was photo-oxidized at moderate frequency giving a band at 22740 cm.$^{-1}$ (4400 Å.). So also Michler's ketone gives a band at 19700 cm.$^{-1}$ (5070 Å.). It is evident from the examples here given that the number and variety of the odd ions that can be produced by photo-oxidation, and studied spectroscopically, can be indefinitely extended. Except in rare cases these semiquinone forms cannot be studied under ordinary conditions of solvent and temperature. Many of them can, however, be obtained by photo-oxidation at higher temperatures, in a sufficiently rigid solvent such as glycerol or triethanolamine at −80°. Even at room temperature they may be observed in supercooled dextrose, although it is difficult to melt the dextrose and dissolve the solute without a slight caramelization which causes absorption in the near ultraviolet and the violet.

It is not to be supposed that photo-oxidation occurs more often in rigid than in ordinary media. However, in a fluid medium the electron can return in a very short time. Nevertheless, in the fluid medium during this short time in which the electron is removed, other processes may occur which lead to the decomposition of the original substances. Most of the substances discussed in this paper must be kept in dark bottles, and it seems probable that in their photo-chemical decomposition, the initial process is the ejection of an electron. On the other hand, in the gaseous state, where, because of the low dielectric constant, the energy required for the ejection of an electron is much greater, it would take light of very high frequency to cause such an ejection.

Summary

A further study is made of the odd ions and radicals produced by the illumination of many types of organic substances in a rigid solvent. The spectra of these substances have been determined with a view to the ultimate formulation of the laws of color in odd molecules. That these laws are different from those for ordinary molecules is shown by the color of the odd ion of *m*-phenylenediamine and perhaps by the remarkable auxochrome effects found in substituted benzenes. The role of electron ejection in ordinary photochemical processes is discussed.

BERKELEY, CALIFORNIA RECEIVED SEPTEMBER 13, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY]

The Vapor Phase Nitration of Toluene

BY J. L. BULLOCK AND E. T. MITCHELL

In a previous report[1] it was shown that the vapor phase nitration of toluene by means of 70% nitric acid proceeded in the neighborhood of 150° with the formation of ortho, meta and para-nitrotoluenes in somewhat different proportions than are recorded for the liquid phase nitration. Specifically, Holleman and others[2] obtained in the liquid phase at 30° values of 58.8% ortho, 4.4% meta and 36.8% para, while the reaction in the vapor phase at 150° gave 55.8% ortho, 5.0% meta and 39.2% para.

The present study is an extension of the previous work under varying experimental conditions to determine in particular the effect of changes in temperature and of concentration of nitric acid on the relative proportions of the three isomers. In addition the analytical results obtained previously have been checked by subjecting the present mixtures to two other independent methods of analysis.

Experiments have been carried out in which the concentration of the nitric acid was varied from 70 to 90%, the amounts being adjusted so that the ratio of nitric acid to toluene remained constant. This variation caused an increase in the over-all conversion to mononitrotoluene from 39 to 74%, but had only a slight effect on the ratio of the isomers. Some tendency toward an increased percentage of the para compound was noted.

Holleman and Van den Arend[3] have observed that a change in temperature from −30 to +60° in the liquid phase nitration causes a decrease in the percentage of *p*-nitrotoluene formed. In the present series of experiments the temperature in the vapor phase nitration was varied between 150 and 350° to discover the effect of temperature change on the isomer ratio in the gas phase reaction. Since a greater tendency for oxidation and other side reactions, which might have upset the true isomer ratios, was encountered at the higher temperatures and also to a less extent at the higher acid concentrations, a program of identification and analysis of the by-products was carried out. Using 70% nitric acid it was found that proportion of the by-products to the mononitrotoluene was so high as to make specification of the isomer ratios unreliable above 250°. In the range 150 to 250°, the observed change in the isomer ratio was noted to be within the range of experimental error, indicating that the rates of gaseous nitration have similar temperature coefficients.

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[1] J. L. Bullock and E. T. Mitchell, THIS JOURNAL, **63**, 3230 (1941).

[2] (a) A. F. Holleman, *Rec. trav. chim.*, **18**, 268 (1899); **33**, 1 (1914); (b) C. K. Ingold, A. Lapworth, E. Rothstein and D. Ward, *J. Chem. Soc.*, 1959 (1931).

[3] A. F. Holleman and M. J. Van den Arend, *Rec. trav. chim.*, **28**, 408 (1909).

TABLE I

VAPOR PHASE NITRATION OF TOLUENE

In all runs the ratio was 1.67 moles of nitric acid to 1 mole of toluene. The second eutectic temperature was obtained by adding 2.2% *m*-nitrotoluene to the original mixtures.

Temp., °C.	Init. f. p., °C.	First eutectic temp., °C.	Second eutectic temp., °C.	Percentage *ortho*	Percentage *meta*	Percentage *para*	Percentage yield[b] Oxid. prod.	Percentage yield[b] Dinitro-toluenes	Percentage yield[b] Mononitro-toluenes
				70% HNO_3					
150[a]	7.1	−18.3	−19.3	55.9	5.1	39.0	...	...	35.0
150	7.6	−18.3	−19.7	55.7	5.0	39.3	0.2	...	39.0
150[a]	7.6	−18.3	−19.7	55.7	5.0	39.3	...	...	43.0
250	7.3	−18.3	−19.6	55.9	5.0	39.1	0.3	...	27.0
350	...	....	....	..	...	..	5.0	0.6	17.0
				80% HNO_3					
150	8.3	−18.1	−19.5	55.2	4.8	40.0	0.3	0.3	63.0
200	8.1	−18.0	−19.3	55.7	4.5	39.8	0.4	0.3	60.0
250	8.2	....	....	..	...	39.8	0.7	0.4	57.0
				90% HNO_3					
150	9.6	−18.0	−19.4	54.4	4.5	41.1	0.4	1.2	74.0
200	9.3	−18.0	−19.3	54.7	4.5	40.8	1.0	2.3	67.0
250	9.2	....	....	..	...	40.7	2.7	3.0	60.0

[a] Rate of flow through the reaction chamber based on toluene was 3 ml. per min. for the first run, 0.2 ml. per min. for the third run and 1 ml. per min. for all other runs. [b] Based on toluene employed.

The above results cannot be accounted for on the basis of an equilibrium between the isomers, for Norris and Turner[4] have shown that such an equilibrium does not occur under these conditions.

The by-products were analyzed by fractional distillation and crystallization methods, and the following organic substances were identified: 2,4-dinitrotoluene, *p*- and *o*-nitrobenzoic acids, 2,4,6-trinitro-3-hydroxybenzoic acid (comprised 50–60% of the acid organic by-product) and 2,4-dinitrobenzoic acid.

In other experiments at 150° using 70% nitric acid, the molar nitric acid–toluene ratio was varied from 1:1, which gave an over-all yield of 15% mononitrotoluenes, to 4:1, which gave a yield of 62%, but there was no measurable alteration in the relative proportions of the three isomers. The rate of flow of toluene through the reaction chamber was also varied from 0.2 to 3.0 ml. per minute without appreciable change in the isomer ratio.

A summary of the actual results is shown in Table I.

Experimental

The apparatus and technique of operation and purification of the product have been described in the previous report.[1] The nitric acid and toluene employed were also the same as there specified. In addition, for some of the analytical standardizations, pure samples of the three mononitrotoluenes were required. Eastman Kodak Co.'s best grade was used: ortho, b. p. 110–112° (20 mm.); meta, m. p. 15.2–15.8°; para, m. p. 51.5–51.7°.

The products of the reaction were analyzed for total mononitrotoluene content using titanous chloride,[5] which was standardized against pure *p*-nitrotoluene. In addition the aqueous extract was analyzed for nitrate,[6] nitrite and acidic organic material. Based on these analyses, an over-all nitrogen recovery of 94–97% was obtained, the remainder being largely nitric oxide which did not condense.

Analysis of the Isomeric Mononitrotoluenes.—The principal method used for estimating the percentages of each of the isomers present in the purified sample was the freezing-point technique of Gibson, Duckham and Fairbairn,[7] following the procedure of Philip.[8] Standard freezing point–composition curves were developed from determinations on known mixtures of the pure isomers. It was necessary to seed the melts to obtain correct freezing temperatures.

Two of the runs were also analyzed by supplementary methods: (1) that based on the solubilities of the nitrobenzoic acids, according to the directions of Holleman[2a] and Baker,[9] and (2) the bromination technique for the determination of the meta isomer.[10] This last method was found by standardization to give results about 10% too low. When a correction was applied for this, results as to *m*-nitrotoluene content by all three methods checked within an absolute value of 0.2%.

Acknowledgment.—We are greatly indebted to Holy Cross College for having generously placed at our disposal the facilities of its laboratories.

Summary

1. The isomer ratio in the gas phase nitration of toluene is fairly constant at 55% ortho, 5% meta and 40% para-nitrotoluene over a rather wide range of experimental conditions.

2. By-products of the nitration process have been isolated and identified. They represent expected multiple nitration and oxidation products.

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(4) J. F. Norris and H. S. Turner, THIS JOURNAL, **61**, 2128 (1939).

(5) I. M. Kolthoff and N. H. Furman, "Volumetric Analysis," John Wiley and Sons, New York, N. Y., 1929, Vol. II, p. 504.

(6) F. C. Bowman and W. W. Scott, *Ind. Eng. Chem.*, **7**, 766 (1915).

(7) W. H. Gibson, R. Duckham and R. Fairbairn, *J. Chem. Soc.*, **121**, 270 (1922).

(8) J. C. Philip, *ibid.*, **83**, 814 (1903).

(9) J. W. Baker, *ibid.*, **125**, 2468, 2469 (1926); **126**, 568 (1927).

(10) H. Ditz, *Z. angew. Chem.*, **37**, 873 (1899); **38**, 897 (1899); **42**, 1050 (1900); A. W. Francis and A. J. Hill, THIS JOURNAL, **46**, 2498 (1924).

3. The reliability of the method of analysis using measurements of the freezing point which are employed in this and in our preceding investigation, has been confirmed by measurements made by two other independent methods.

WORCESTER, MASS. RECEIVED MARCH 16, 1943

[CONTRIBUTION OF THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

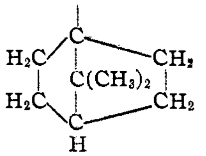
Reactions of Atoms and Free Radicals in Solution. V. The Non-coplanar Free 1-Apocamphyl Radical

BY M. S. KHARASCH, FRANCES ENGELMANN AND W. H. URRY

All free radicals of type $R_1R_2R_3C\cdot$ which have hitherto been described, whether they be of long half-life period (expressed in years) or of short half-life period (expressed in thousandths of a second), yield optically inactive products of the form $R_1R_2R_3CX$. Presumably this optical inactivity is due to the ability of the free radical to assume a coplanar configuration in at least one phase of its internal vibrations. Note, for instance, the optical inactivity of the 1,2-dichloro-2-methylbutane prepared by the chlorination of 1-chloro-2-methylbutane,[1] a reaction in which the free radical $(CH_3)(C_2H_5)\dot{C}CH_2Cl$ is an intermediate. It is, however, possible to prepare free radicals which cannot assume a coplanar configuration. Since the behavior of such free radicals in solution is of considerable theoretical interest, an investigation of the methods of preparing a number of these substances has been undertaken. The present paper contains evidence for the existence of the non-coplanar free 1-apocamphyl radical. Other radicals of this type will be reported in a future publication, and the theoretical significance of the findings will there be discussed.

Preparation and the Reactions of the Free 1-Apocamphyl Radical.—The free 1-apocamphyl radical was generated in carbon tetrachloride solution by heating the peroxide of apocamphane-1-carboxylic acid. The following products, in the quantities indicated, were isolated.[2]

R = 1-apocamphyl radical =



$$(\mathrm{RCOO{-}})_2 \xrightarrow{\mathrm{CCl_4}} \underset{(36\%)}{\mathrm{RCl}} + \underset{(9\%)}{\mathrm{RR}} + \underset{(50\%)}{\mathrm{RCOOR}} + \underset{(5\%)}{\mathrm{RCOOH}} + \mathrm{C_2Cl_6}$$

The peroxide of apocamphane-1-carboxylic acid is unusually stable; it is completely decomposed only after being heated for about twenty hours in the carbon tetrachloride solution. The separation of the solvent and of the various reaction products was quite difficult. A vacuum technique had to be developed to separate the carbon tetrachloride from 1-chloroapocamphane and hexachloroethane, both of which are extremely volatile. These last two substances could not be separated by physical means, but it was found possible to destroy the hexachloroethane without breaking down the 1-chloroapocamphene, since the latter compound[3] is not readily attacked by inorganic bases. However, in spite of the difficulties mentioned, the course of the reaction was most satisfactory; no tar was formed, and it was possible to account quantitatively for all the peroxide used (see above).

The formation of all the products found is probably best accounted for by the mechanism

$R\cdot$ = 1-apocamphyl radical

(1) $\mathrm{RCOO{-}OOCR} \longrightarrow \mathrm{R\cdot} + \mathrm{CO_2} + \mathrm{RCOO\cdot}$
(2) $\mathrm{R\cdot} + \mathrm{CCl_4} \longrightarrow \mathrm{RCl} + \mathrm{Cl_3C\cdot}$
(3) $\mathrm{R\cdot} + \mathrm{RCOO\cdot} \longrightarrow \mathrm{RCOOR}$
(4) $\mathrm{R\cdot} + \mathrm{RCOO{-}OOCR} \longrightarrow \mathrm{RCOOR} + \mathrm{RCOO\cdot}$
(5) $\mathrm{R\cdot} + \mathrm{R\cdot} \longrightarrow \mathrm{RR}$
(6) $\mathrm{R\cdot} + \mathrm{RCOO{-}OOCR} \longrightarrow \mathrm{RR} + \mathrm{CO_2} + \mathrm{RCOO\cdot}$
(7) $\mathrm{RCOO\cdot} \longrightarrow \mathrm{R\cdot} + \mathrm{CO_2}$
(8) $\mathrm{Cl_3C\cdot} + \cdot\mathrm{CCl_3} \longrightarrow \mathrm{C_2Cl_6}$

In view of the high stability of the peroxide and the consequent low concentration of the free radical $R\cdot$ at any one moment, formation of the ester and the dimer (bi-1-apocamphyl), according to reactions (4) and (6), seems to us more probable than their formation according to reactions (3) and (5).[4]

The type of decomposition given above is characteristic only for stable organic peroxides. Since the concentration of free radical resulting from the decomposition of such peroxides is at no time large, and since, in the experiments described, the yield of ester is about the same as the yield of chloro compound, the energy of activation required to remove a chlorine atom from carbon tetrachloride (reaction (2)) is probably about the same as that required to cleave the peroxide (reaction (3)).[5] Furthermore, the cleavage of the

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[1] Kharasch and Brown, THIS JOURNAL, **61**, 2142, 3432 (1939); **62**, 925 (1940); Brown, Kharasch and Chao, *ibid.*, **62**, 3435 (1940).

[2] As expected, the molar yield of hexachloroethane was half of that of 1-chloroapocamphane.

[3] Bartlett and Knox, THIS JOURNAL, **61**, 3184 (1939).

[4] Another possible method of forming the ester RCOOR is by unimolecular decomposition of the peroxide into one molecule of carbon dioxide and one molecule of ester.

[5] Due allowance must of course be made for the fact that the solvent is at a higher concentration than the peroxide. The cleavage of the peroxide by the free 1-apocamphyl radical probably requires less activation energy than is required for the removal of a chlorine atom from a molecule of carbon tetrachloride.