mixed with acetyl peroxide, the gaseous mixture decomposed, and the products analyzed. The results are summarized in Table III. It can be seen that the iodine does not react with acetyl peroxide (the rate constant for the unimolecular decomposition is unaffected by the presence of iodine vapor). However, iodine reacts efficiently with methyl radicals, and consequently the ratio $2C_2H_6/CO_2$ is reduced effectively to zero as the partial pressure of iodine vapor is raised to 0.23 mm. These results prove conclusively that reaction 4 does not take place and, therefore, we conclude finally that the formation of ethane in the liquid phase decomposition must be attributed to a cage reaction.

TABLE III

DECOMPOSITION OF DIACETYL PEROXIDE IN THE PRESENCE OF IODINE VAPOR

Gaseous phase, $T = 461°K.$; flow system; partial pressure of peroxide about 0.1 mm.; partial pressure of the carrier gas (toluene) about 15 mm.

Partial pressure of I_2, mm.	$2C_2H_6/CO_2$	k, sec.$^{-1}$
0.00	1.00	1.95
.064	0.034	1.74
.12	.020	1.69
.23	.0004	1.80

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The Thermal Decomposition of Triazobenzene in Solution

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The thermal decomposition of azo compounds such as 2,2'-azo-bis-isobutyronitrile in solution involves the splitting out of nitrogen and the production of two monoradicals. It would be expected that triazobenzene would decompose to give a diradical and nitrogen.

$$\mathrm{PhN_3} \longrightarrow \mathrm{PhN}< + \mathrm{N_2}$$

Evidence for such a mechanism comes from studies of the products of decomposition of triazobenzene in benzene and *p*-xylene.[1] Bertho showed that azobenzene and aniline were formed, the azobenzene probably arising from combination of two diradicals and the aniline from hydrogen abstraction reactions with the solvent. A kinetic study of the decomposition in solution has now been made to obtain support for such a mechanism and to establish the kinetic constants for the reaction. In addition an attempt has been made to use triazobenzene as a diradical source in the polymerization of methyl methacrylate.

Experimental

Triazobenzene was prepared from phenylhydrazine by the method of "Organic Syntheses."[2] It was twice distilled at reduced pressure in an atmosphere of nitrogen to give a pale yellow product. It was stored at 0°.

Tetrahydronaphthalene was distilled twice at reduced pressure in an atmosphere of nitrogen, and stored under dry nitrogen at 0°.

Nitrobenzene was subjected to crystallization and distilled at reduced pressure.

Methyl methacrylate (Rohm and Haas Company) was freed from inhibitor with sodium hydroxide solution, washed and dried, and distilled at 100 mm. pressure in an atmosphere of nitrogen. It was transferred to a vacuum apparatus and degassed four times and distilled twice *in vacuo*. It was stored at −80°.

Procedure.—Solutions of triazobenzene in the solvent, tetrahydronaphthalene or nitrobenzene, were made up over a wide concentration range. Five ml. of solution was placed in the apparatus consisting of a reservoir of volume 15 ml. attached to a capillary mercury manometer. The solution was thoroughly degassed and the apparatus sealed off. The reaction was followed by the pressure increase due to evolution of nitrogen; about 0.95 mole nitrogen was evolved per mole of triazobenzene decomposed. No correction for gas evolution from the solvent was necessary. Measurements were made over the temperature range 105–145°, the thermostat being controlled to ±0.1°. The manometer was heated to 5° above the temperature of the reservoir; under this condition the vapor phase reaction was negligible compared with the reaction in solution. Initial rates of reaction were used to determine the order of reaction and the dependence of rate on temperature. In two reactions which were followed to completion, a first-order law was accurately obeyed.

In experiments with methyl methacrylate, sealed tubes were used, and these were cooled and opened up to a manometer after definite time intervals to determine the amount of nitrogen formed. In parallel experiments the rate of polymerization of the methyl methacrylate was measured by precipitating the long chain polymer in methanol.

Results and Discussion

The rates of decomposition of triazobenzene in tetrahydronaphthalene and nitrobenzene were determined for the concentration range 0.0288–0.36 mole/l. triazobenzene at a temperature of 130°. The results are given in Table I. The rate of reaction is clearly proportional to the concentration of triazobenzene in both solvents. It is thus shown that the decomposition is a unimolecular process, almost certainly of the form

TABLE I

Concn. of triazobenzene, mole/l.	Rate in tetrahydronaphthalene $\times 10^6$, mole/l./sec.	Rate in nitrobenzene $\times 10^6$, mole/l./sec.
0.36	2.28	2.33
.144	0.936	0.950
.072	.482	.475
.0288	.210	.202

$$\mathrm{PhN_3} \longrightarrow \mathrm{PhN}< + \mathrm{N_2}$$

and does not involve a bimolecular process of the type

$$\mathrm{2PhN_3} \longrightarrow \mathrm{2N_2} + \mathrm{PhN{=}NPh}$$

nor an induced decomposition such as is observed with benzoyl peroxide.[3] Reaction rates were nearly the same for the two solvents, tetrahydronaphthalene and nitrobenzene, and it seems that the solvent does not take any part in the first step of the decomposition other than solvating the reactant to some extent.

The results for the dependence of first-order rate constant k on temperature are summarized in Table II. For tetrahydronaphthalene as solvent they can be expressed in the form

$$k = 2.51 \times 10^{12}\, e^{-32{,}500/RT}$$

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(1) A. Bertho, *Ber.*, **57B**, 1138 (1924).

(2) *Org. Syntheses*, **22**, 96 (1942).

(3) K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946).

TABLE II

Temp., °C.	k(sec.$^{-1}$) × 10^6 in tetrahydronaphthalene	k(sec.$^{-1}$) × 10^6 in nitrobenzene
105	0.40	0.35
115	1.34	1.20
130	6.01	6.25
145	24.7	25.0

and for nitrobenzene

$$k = 8.68 \times 10^{12} e^{-33,500/RT}$$

The experimental error in the activation energy is estimated at ±0.4 kcal./mole and therefore the difference between the two activation energies is probably significant. Alder and Leffler[4] have shown that the decomposition of phenylazotriphenylmethane proceeds at roughly the same rate in a number of solvents, but that this is due to compensating effects of activation energies and A factors. They explained their results in terms of the desolvation of the azo compound before reaction. Only two inert solvents have been used in the present work, but it appears that a similar effect may be operative in the decomposition of triazobenzene.

With methyl methacrylate as solvent, the evolution of nitrogen was many times more rapid than with the other two solvents and it is concluded that the methyl methacrylate is taking a definite part in the reaction. Triazobenzene is known to react with compounds such as styrene to give diphenyltriazoline[5] and it is probable that a similar reaction occurs with methyl methacrylate, the triazoline then breaking down with the splitting off of nitrogen. This second reaction may also proceed through a diradical intermediate and, if so, the production of very small amounts of polymer would indicate that the diradicals are not efficient in initiating the production of long chain polymer. The uncertainties in the detailed nature of the reaction, however, make it unwise to attempt to reach any firm conclusion.

The author is grateful to Professor F. S. Dainton of the University of Leeds for suggesting the use of triazobenzene as a possible source of diradicals.

(4) M. G. Alder and J. E. Leffler, THIS JOURNAL, **76**, 1425 (1954).

(5) L. Wolff, *Ann.*, **394**, 69 (1912).

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The Fluoroplatinates. III. The Alkali Fluoroplatinates

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Of the alkali fluoroplatinates, the potassium, rubidium and cesium salts have been previously prepared. Schlesinger and Tapley[2] prepared the potassium salt by heating finely divided platinum with 3KF·HF·PbF$_4$. The salt was found to be a yellow crystalline compound, sparingly soluble in water and having a characteristic absorption band in the ultraviolet region of the spectrum.

Sharpe[3] prepared potassium, rubidium and cesium fluoroplatinates by treatment of the chloroplatinates with bromine trifluoride. The crystal structures of these salts were determined.

The preparation of the lithium, sodium and ammonium fluoroplatinates has not been previously reported. This paper concerns the preparation and some of the properties of all the alkali fluoroplatinates.

Experimental

Reagents.—Lanthanum fluoroplatinate was prepared as previously reported.[4] All other reagents were C.P. grade.

Analyses.—The alkali content of the salts was determined by means of a Beckman flame spectrophotometer. For the ammonium salt, Nessler's solution was used. In all analyses, the samples were first dried at 100° under an atmospheric pressure of 625 mm.

Solubility.—The solubilities of the alkali fluoroplatinates were determined at 25 ± 0.5°. A Warburg apparatus was used. Agitation for 24 hours in polyethylene bottles was considered adequate for the establishment of equilibrium conditions. The solubilities were determined in grams per 100 ml. of solution.

Density.—The densities of the alkali salts were determined at 25 ± 0.5°. A 4.5-ml. pycnometer was used with toluene redistilled from sodium carbonate as the inert liquid.

Absorption Spectra.—The absorption spectrum study of these salts was performed with a model DU Beckman spectrophotometer using matched 1-cm. cells.

The Alkali Fluoroplatinates.—The potassium, rubidium and cesium fluoroplatinates were prepared by simple metathesis since they are sparingly soluble. In each case a saturated solution of the respective alkali nitrate was added to a 0.02 M lanthanum fluoroplatinate solution. The precipitates were centrifuged, washed and then purified by recrystallization from hot water.

Sodium fluoroplatinate was prepared by the titration of sodium hydroxide and lanthanum fluoroplatinate. The equation for the reaction is $6NaOH + La_2(PtF_6)_3 \rightarrow 3Na_2PtF_6 + 2La(OH)_3$. A 1 N sodium hydroxide solution was added slowly to the lanthanum fluoroplatinate solution. Lanthanum hydroxide precipitated immediately. The addition of the alkali was continued until the formation of any new precipitate could not be detected. The solution was centrifuged to pack the lanthanum hydroxide and then more alkali was added to the supernatant liquid until precipitation appeared complete. The solution was again centrifuged. Several drops of the supernatant liquid were placed in each of two holes of a black color reaction plate. To one of these a drop of sodium hydroxide was added and to the other a drop of lanthanum fluoroplatinate solution. If no precipitate was evident in either instance then the endpoint was regarded as reached. The solution was filtered and it was evaporated nearly to dryness in a vacuum oven at 75° under a pressure of 625 mm. The concentrated solution was then placed in a water-bath at 5° until precipitation was complete. The salt was obtained by centrifugation, was then washed and purified by recrystallization from hot water.

By titration of ammonium hydroxide and lanthanum fluoroplatinate and following the procedure just described, ammonium fluoroplatinate was obtained.

Lithium fluoroplatinate was prepared in the same manner but its isolation free of hydrolytic products was not possible. The evaporation of the lithium solution produced no crystalline product until an almost completely anhydrous state was reached. Upon complete dehydration, well defined yellow crystals were present but were mixed with a white residue which was shown to be lithium fluoride. Measurement of the absorption spectrum of a solution made from the yellow crystals confirmed the indication that hydrolysis of the fluoroplatinate ion had occurred. The characteristic maxima of the fluoroplatinate ion at 275 and 318 mμ were absent. A new absorption curve with a maximum at 263 mμ was obtained. Further investigation of this hydrolysis reaction is being carried out.

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(1) Abstracted from a portion of the thesis submitted by Thomas E. Wheeler in partial fulfillment of the requirements for the degree of Master of Science.

(2) H. Schlesinger and M. Tapley, THIS JOURNAL, **46**, 276 (1924).

(3) A. G. Sharpe, *J. Chem. Soc.*, 197 (1953).

(4) T. P. Perros and C. R. Naeser, THIS JOURNAL, **75**, 2516 (1953).