Chemistry

1961

SovietRxiv

Abstract

Full Text

Chemistry

I. P. Gragerov and M. Ya. Turkina

Investigation of Transformations of Phenyl Radicals in Solution by Isotopic and Mass-Spectrometric Methods

(Presented by Academician M. I. Kabachnik on 2 VI 1961)

Homolytic reactions may proceed by two different mechanisms: through free radicals or by formation of a reaction complex, the decomposition of which gives products without the participation of free radicals. The choice between these two mechanisms presents considerable difficulties and has until now required extensive investigations of each individual reaction.

In the present work a variant of the isotopic method is set forth in combination with the mass-spectrometric method, facilitating this choice and making it possible simply to decide the question of the mechanism of homolytic reactions in which compounds with phenyl residues participate. The reactions studied were carried out in benzene, which is a mixture of the isotopic varieties C_6D_6 and C_6H_6 (as well as smaller amounts of C_6D_5H, $C_6D_4H_2$, etc., but not C_6H_5D), or in cyclohexanes C_6D_{12} and C_6H_{12}.* The solvent before and after the reaction, as well as the products, were analyzed by low-voltage mass spectrometry (^{1}), which made it possible to determine the amounts of molecular varieties with one, two, three, etc. deuterium atoms. In these experiments we took from 0.5 to 1 mole of substrate per 1 mole of solvent.

It was found that photolysis of iodobenzene both in the presence and in the absence of copper, and thermal decomposition of benzoyl peroxide, when carried out in the medium $C_6D_6 + C_6H_6$, lead to the appearance in the solvent of benzene C_6H_5D, which was absent before the reaction. The same transformations, when carried out in the medium of cyclohexanes $C_6D_{12} + C_6H_{12}$, lead to the appearance in the solvent of benzenes C_6H_5D and C_6H_6, which were not present in the original cyclohexane.**

Bearing in mind that the free-radical mechanism of iodobenzene photolysis (^{2,3}) and of the thermal decomposition of benzoyl peroxide (^{4}) is well substantiated, and that the behavior of free radicals $C_6H_5\cdot$ should not depend on the source of their formation, one may suppose that all other reactions involving these radicals will likewise lead to the appearance of previously absent C_6H_5D molecules when carried out in the medium $C_6D_6 + C_6H_6$, and to the appearance of C_6H_5D and C_6H_6 molecules when carried out in the medium $C_6D_{12} + C_2H_{12}$. The cause of the appearance of C_6H_5D molecules may be the reaction:

$$C_6H_5\cdot + C_6D_6 \rightarrow C_6H_5D + C_6D_5\cdot, \tag{1}$$

the existence of which had been assumed earlier (see, for example, ([3,6,8,11])), or the reaction of C_6H_5 radicals with hydrodiphenyl, formed upon addition of phenyl radicals to benzene:

$$C_6H_5\cdot + D{-}C_6D_5 \rightarrow C_6H_5{-}C_6D_5\cdot;$$

$$C_6H_5\cdot + C_6H_5{-}C_6D_5\cdot \rightarrow C_6H_5D + C_6H_5{-}C_6D_5, \tag{2}$$

as well as a reaction analogous to (1) with cyclohexane:

$$C_6H_5\cdot + C_6D_{12} \rightarrow C_6H_5D + C_6D_{11}\cdot. \tag{3}$$

The appearance of C_6H_6 molecules is apparently caused by reactions analogous to (3) with C_6H_{12} and with other participants or products of the transformations under study. For reactions occurring in a reaction complex, on the contrary, one cannot expect that the phenyl group from the complex could abstract hydrogen from benzene or cyclohexane with the formation of benzenes C_6H_5D and C_6H_6.

We propose to use this distinction between free-radical processes and processes occurring in a reaction complex in order to distinguish reactions of these two types from one another. A study of the thermal decomposition of chlorobenzenediazonium and borofluorobenzenediazonium, the mechanism of which had remained unclear until now ([5]), showed that, when this reaction is carried out in a $C_6D_6 + C_6H_6$ medium, the solvent after the experiment contains no C_6H_5D molecules, and when it is carried out in a $C_6D_{12} + C_6H_{12}$ medium, the solvent after the experiment contains no C_6H_5D or C_6H_6 molecules. It follows from this that these reactions do not have a free-radical mechanism.

An analogous conclusion for the thermal decomposition of the double salt $(C_4H_5N_2)_2ZnCl_4$ was drawn in work ([6]) by means of another variant of the isotope method. The thermal decomposition of $C_6H_5N_2BF_4$ apparently also does not proceed through $C_6H_5^+$ ions, since these ions, analogously to Alk^+ ions,

---

* These benzenes and cyclohexane were prepared by mixing highly deuterated and light preparations of both substances.

** Control experiments showed that, upon irradiation of benzene $C_6D_6 + C_6H_6$ or cyclohexane $C_6D_{12} + C_6H_{12}$ with ultraviolet light, both in the absence and in the presence of copper, benzenes C_6H_5D and C_6H_6 are not formed.

which abstract hydrogen from Alk—H molecules (7), should have abstracted deuterium from C_6D_6 and C_6D_{12} molecules, giving benzene C_6H_5D, which did not occur. Thus, both diazonium salts studied decompose in a reaction complex. Isotopic analysis of the products of the reactions studied confirmed the conclusions obtained from analysis of the solvent and made it possible to clarify certain important details of the mechanism.

The diphenyls obtained in the photolysis of iodobenzene or in the thermal decomposition of benzoyl peroxide in a $C_6D_6 + C_6H_6$ medium contained less deuterium than would have been expected if they were formed only by the reaction

$$C_6H_5 \cdot + C_6D_6 \xrightarrow{-D\cdot} C_6H_5{-}C_6D_5, \qquad (4)$$

but had almost the same ratio of isotopic varieties with 5, 4, and 3 deuterium atoms as did the benzene solvent after the reaction. Consequently, the diphenyls were formed by two pathways—by reaction (4) and as a result of recombination of two light $C_6H_5\cdot$ radicals in photolysis experiments (probably on the surface of copper), or as a result of interaction of these radicals with unreacted benzoyl peroxide (and also, apparently, in the intramolecular decomposition of benzoyl peroxide). Similar results, obtained by another variant of the isotope method, were reported in works (3,8,9).

The diphenyl obtained in the thermal decomposition of borofluorobenzenediazonium in a $C_6D_6 + C_6H_6$ medium contained as much deuterium as it should have if formed by combination of the phenyl residues of the diazonium salt and the solvent. The ratio of forms with five, four, and three deuterium atoms was close to that of the original benzene. Fluorobenzene contained no deuterium. Precisely such a composition of the products was to be expected for a reaction proceeding in a reaction complex, without liberation of $C_6H_5\cdot$ radicals (or $C_6H_5^+$ ions), which once again confirms

this mechanism. In diphenyl obtained by thermal decomposition of phenyldiazonium chloride in a medium of $C_6D_6 + C_6H_6$, the ratio of forms with 5, 4, and 3 deuterium atoms likewise corresponded to the initial benzene, but the diphenyl contained an increased amount of the C_6H_5—C_6H_5 form, which indicates the formation of this substance not only by combination of phenyl residues from the salt and the solvent, but also by combination of phenyl residues only from the diazonium salt.

We also studied the oxidation of $C_6D_6 + C_6H_6$ benzene by chromyl chloride (CrO_2Cl_2). In this experiment, 3/4 of the amount of hydrocarbon taken was oxidized. The isotopic composition of the unreacted residue is shown in Table 1, which serves as an example of our isotopic analyses of benzenes.

Table 1

Example of an isotopic analysis of benzene

Isotopic variety of benzene	Content in the initial benzene, %	Content in benzene after the experiment, %
C_6D_6	22.2 ± 0.25	20.74 ± 0.20
C_6D_5H	17.1 ± 0.15	17.12 ± 0.16
$C_6D_4H_2$	5.47 ± 0.05	5.98 ± 0.09
$C_6D_3H_3$	1.00 ± 0.01	1.16 ± 0.04
$C_6D_2H_4$	–	0.25 ± 0.02
C_6DH_5	–	2.17 ± 0.16
C_6H_6	54.0 ± 0.2	52.6 ± 0.3
D, at.-%	40.6 ± 0.5	40.0 ± 0.4

The data of Table 5 show that, after the experiment, a significant number of C_6H_5D molecules appeared in the benzene, and the reaction thus has a free-radical mechanism*.

When considering Table 1, it should be kept in mind that the reaction leading to the appearance of the C_6H_5D molecule (for example, reaction (2)) is not the only pathway for the conversion of C_6H_5 radicals. It competes with the interaction between C_6H_5 and CrO_2Cl_2 and with reaction (4). Therefore the yield of C_6H_5D molecules is relatively small.

The reaction of metallic magnesium with iodobenzene in a C_6D_6+C_6H_6 medium on heating gave results that also indicate a free-radical mechanism: benzene distilled off from the reaction mixture (benzene a) contained C_6H_5D molecules. Vacuum sublimation of the residue after distillation of the benzene gave diphenyl (diphenyl a), containing less deuterium than would be expected if it were formed only by reaction (4), but with a ratio of the amounts of forms with 5, 4, and 3 deuterium atoms close to this ratio in benzene after the reaction. The residue from sublimation of the diphenyl, after treatment with water, gave a new portion of benzene (benzene b), which contained no deuterium, and a new portion of diphenyl (diphenyl b), which contained almost no deuterium.

These data can be explained as follows: the reaction of magnesium with C_6H_5J gives C_6H_5MgJ, with intermediate formation of C_6H_5 radicals that abstract deuterium from the medium with formation of C_6H_5D benzene. Diphenyl a is formed by two different pathways–by reaction (4) and by the reaction

$$C_6H_5MgJ + C_6H_6J \to C_6H_5\text{—}C_6H_5 + MgJ_2.$$

Benzene b arises in the interaction of water with C_6H_5MgJ that did not enter into reaction with iodobenzene. The absence of deuterium in it indicates the absence, under the experimental conditions, of isotopic exchange between C_6H_5MgJ and C_6D_6 (also not found in [13]). Finally, diphenyl b is probably formed according to the scheme:

$$C_6H_5J \xrightarrow{+C_6H_5;\,-H^{\cdot}} C_6H_5—C_6H_4J \xrightarrow{+Mg} C_6H_5—C_6H_4MgJ \xrightarrow{H_2O} C_6H_5—C_6H_5.$$

We also studied the Fittig-Wurtz reaction between 2.25 g of iodobenzene and 0.5 g of metallic sodium in a medium of 1.13 g of $C_6D_6 + C_6H_6$ benzene in the cold. The results of isotopic analysis of the benzene after the reaction and of the diphenyl obtained are presented in Table 2 in comparison with the isotopic composition calculated for the case of a statistical distribution of deuterium over all isotopic varieties of both of these substances. The calculation was carried out by the Brodsky formula (10). The data obtained show that both the benzene

Table 2

Isotopic composition of benzene and diphenyl obtained in the interaction of C_6H_5J with sodium in a $C_6D_6 + C_6H_6$ medium

Isotopic varieties of benzene	Content in starting benzene, %	Content in benzene after experiment, %	Calculated, %	Isotopic varieties of diphenyl	Content in obtained diphenyl, %	Calculated, %
C_6D_6	6.61 ± 0.43	–	–	$C_{12}H_5D_5$	–	–
C_6D_5H	2.97 ± 0.20	–	–	$C_{12}H_6D_4$	0.09 ± 0.01	0.02
$C_6D_4H_2$	0.58 ± 0.05	0.083 ± 0.02	0.02	$C_{12}H_7D_3$	0.63 ± 0.06	0.37
$C_6D_3H_3$	–	0.67 ± 0.02	0.39	$C_{12}H_8D_2$	4.59 ± 0.25	4.56
$C_6D_2H_4$	–	4.65 ± 0.4	4.46	$C_{12}H_9D$	26.3 ± 0.7	27.6
C_6DH_5	–	25.7 ± 0.4	27.0	$C_{12}H_{10}$	63.3 ± 0.7	67.6
C_6H_6	89.9 ± 0.5	69.0 ± 0.5	68.1			
D, at.-%	9.84 ± 0.64	6.2 ± 0.34	–	D, at.-%	3.78 ± 0.13	–

* Another possible explanation—the appearance of C_6H_5D molecules as a result of isotopic exchange between light and heavy benzene under catalysis by HCl formed during the reaction—was rejected by control experiments under conditions more severe than the reaction conditions. The significance of the participation of C_6H_5 radicals, discovered by us, for understanding the mechanism of the Etard reaction will be discussed in another paper.

and the diphenyl obtained in this reaction have an isotopic composition almost exactly corresponding to the statistical distribution of deuterium.

In view of the fact that our experiments on the photolysis of iodobenzene and the thermal decomposition of benzoyl peroxide in a $C_6D_6 + C_6H_6$ medium showed that in radical processes the statistical distribution of deuterium in benzene is far from being attained, these results cannot be explained by a radical mechanism of the Fittig-Wurtz reaction. They are well explained by the assumption of the intermediate formation of phenylsodium, for which rapid isotopic exchange of hydrogen for deuterium of heavy benzene is very probable (^{11}). The reaction may be represented by the following scheme:

$$C_6H_5J + 2Na \rightarrow C_6H_5Na + NaJ.$$

$$C_6H_5Na + C_6D_6 \rightarrow \text{heavy } C_6H_5Na + \text{heavy } C_6H_6$$

(both with statistical distribution of deuterium).

$$\text{Heavy } C_6H_5Na + C_6H_5J \rightarrow \text{heavy } C_6H_5{-}C_6H_5 + NaJ.$$

Such an ionic mechanism was proposed by Razuvaev on the basis of more indirect data (^{11}).

The nonradical mechanism of the Fittig-Wurtz reaction was also confirmed by its study in a cyclohexane $C_6D_{12} + C_6H_{12}$ medium: after the experiment the solvent contained no benzene C_6H_5D, although it did contain benzene C_6H_6 (formed, probably, by the reaction: $2C_6H_5Na \rightarrow C_6H_4Na_2 + C_6H_6$ (^{12})).

In conclusion, we note that the method proposed in this work not only permits the indication of reactions involving free phenyl radicals, but also makes it possible to elucidate details of the mechanism that escape study by other methods. The method described can apparently find broad application in the study of various homolytic processes.

We thank Academician of the Academy of Sciences of the Ukrainian SSR A. I. Brodsky for assistance in the work.

Institute of Physical Chemistry named after L. V. Pisarzhevsky
Academy of Sciences of the Ukrainian SSR

Received
27 V 1961

REFERENCES

1. G. A. Semenov, M. Ya. Turkina, *Zav. lab.*, **24**, 1084 (1958); G. A. Semenov, M. Ya. Turkina, V. V. Torshina, V. I. Karpunin, Collection

of Works of the State Institute of Applied Chemistry, issue 45, L., 1960, p. 133.

2. G. A. Razuvaev, M. A. Shubenko, DAN, **67**, 1049 (1949).
3. G. A. Razuvaev, G. G. Petukhov, A. F. Rekasheva, G. P. Miklyukhin, DAN, **90**, 569 (1953).
4. A. V. Tobolsky, R. B. Mesrobian, *Organic Peroxids*, N.Y.–London, 1954, p. 72; Ch. Walling, *Free Radicals in Solution*, M., 1960, p. 378.
5. U. Waters, *The Chemistry of Free Radicals*, M., 1948, p. 173.
6. G. A. Razuvaev, G. G. Petukhov, B. G. Zateev, DAN, **127**, 803 (1959).
7. G. P. Miklyukhin, *Isotopes in Organic Chemistry*, Kiev, 1961, p. 253, 412.
8. G. A. Razuvaev, G. G. Petukhov, B. G. Zateev, DAN, **127**, 348 (1959).
9. R. I. Milyutinskaya, Kh. S. Bagdasaryan, E. A. Izrailevich, ZhFKh, **31**, 1019 (1957).
10. A. I. Brodsky, *Chemistry of Isotopes*, M., 1957, p. 346.
11. G. A. Razuvaev, G. G. Petukhov, M. A. Shubenko, V. A. Voitovich, *Ukr. khim. zhurn.*, **22**, 45 (1956).
12. U. Waters, *The Chemistry of Free Radicals*, M., 1948, p. 227.
13. I. A. Korshunov, A. P. Batalov, ZhOKh, **29**, 4048 (1959).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.