234. *The Reaction between Diphenylpicrylhydrazyl and 2-Cyano-2-propyl Radicals.*

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[^{14}C]Diphenylpicrylhydrazyl and [^{14}C]azo*iso*butyronitrile have been used in a study of the reaction between the hydrazyl and 2-cyano-2-propyl radicals. About 10% of the consumed hydrazyl is converted into the corresponding hydrazine. The products of the interaction of 2-cyano-2-propyl radicals are formed to some extent even if excess of hydrazyl is present in the solution; this may be due to decomposition of part of the azo-compound by a molecular mechanism rather than to a cage effect. Diphenylpicrylhydrazine also reacts with 2-cyano-2-propyl radicals. There is a rapid exchange of hydrogen atoms between diphenylpicrylhydrazyl and the corresponding hydrazine.

DIPHENYLPICRYLHYDRAZYL has been widely used as a scavenger for free radicals, but the chemical reactions involved are obscure. The simplest way in which the hydrazyl, itself a free radical, could capture another radical is by combining with it to give a tetrasubstituted hydrazine; there is however no evidence that a combination of this sort occurs to any appreciable extent.[1] In some cases the hydrazyl and the second radical might

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[1] Wild, *Discuss. Faraday Soc.*, 1952, **12**, 127.

undergo disproportionation, to give diphenylpicrylhydrazine and an unsaturated product derived from the second radical. This might occur with the 2-cyano-2-propyl radicals generated in the decomposition of azo*iso*butyronitrile but would be most improbable with the phenyl or benzoate radicals derived from benzoyl peroxide. It is known that diphenylpicrylhydrazyl can abstract hydrogen atoms from certain molecules.[2]

Reagents labelled with ^{14}C have been used in a study of the chemistry of diphenylpicrylhydrazyl and results of the work are presented here. Although final conclusions concerning the mechanism of the scavenging action are not yet permissible, there is evidence that in some cases some of the hydrazyl is converted into the corresponding hydrazine. The labelled reagents have been used to effect accurate and sensitive analyses, by the isotope dilution technique, for the products of the interaction of the hydrazyl and radicals of known structure generated at known rates. The chemistry of diphenylpicrylhydrazine has also been studied.

EXPERIMENTAL

The preparation and purification of most of the materials used have been described already.[3] [^{14}C]Diphenylpicrylhydrazyl was prepared from uniformly labelled picryl chloride by Goldschmidt and Renn's method,[4] and picryl chloride by standard methods from uniformly labelled aniline supplied by the Radiochemical Centre, Amersham. The labelling of the hydrazyl was confined to its picryl group. The hydrazyl was finally recrystallized from chloroform–ether. Diphenylpicrylhydrazine was recrystallized from ethyl acetate.

Unless stated otherwise, reactions were carried out in sealed tubes in the complete absence of air. For analyses by isotope dilution, the mixtures were diluted with carrier material in solution; the solvents were removed by distillation at low temperature. The procedures for *iso*butyronitrile and tetramethylsuccinodinitrile have been described already.[3] Diphenylpicrylhydrazine was purified by repeated crystallization from ethyl acetate; its activity reached a steady level after two crystallizations; in routine experiments the hydrazine was recrystallized three times before assay.

All assays were performed by gas counting. In the experimental results, the counting rates are quoted as counts per min. (c/m) for a fixed weight of carbon dioxide. These counting rates are directly proportional to the $^{14}C : {}^{12}C$ ratio in the specimen.

Diphenylpicrylhydrazyl forms a complex with chloroform, and the material[5] crystallized from chloroform–ether has the formula $(C_{18}H_{12}O_6N_5)_3,CHCl_3$. The weights of hydrazyl used in various experiments have been corrected for the chloroform content; the counting rate for the labelled material has been corrected also.

RESULTS

By using [^{14}C]azo*iso*butyronitrile, it has been shown that when the azo-compound is decomposed in the presence of excess of diphenylpicrylhydrazyl significant quantities of tetramethylsuccinodinitrile are formed;[6] a small quantity of *iso*butyronitrile is also produced. The experiments are summarized in Table 1. The weights of tetramethylsuccinodinitrile and *iso*butyronitrile expected in experiments not involving the hydrazyl are quoted from previous work.[3]

TABLE 1.

Expt. no.	1	2	3	4	5
$(:N\cdot CMe_2\cdot CN)_2$ (mg.)	3·2	3·05	5·6	2·7	5·9
$NPh_2\cdot NPc\cdot$ * (mg.)	6·6	13·1	36·9	35·7	30·4
C_6H_6 (c.c.)	1·6	1·5	2·8	1·35	2·0
Time at 60° (hr.)	16	16	16	16	16
$(\cdot CMe_2\cdot CN)_2$ (mg.) : found	0·13	0·22	0·26	0·15	†
,, : expected in absence of $NPh_2\cdot NPc\cdot$	0·58	0·52	0·95	0·46	1·00
Pr^iCN (mg). : found	†	†	†	†	0·005
,, : expected in absence of $NPh_2\cdot NPc\cdot$	0·26	0·24	0·45	0·22	0·47

* Pc = picryl. † Not determined.

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[2] Braude, Brooke, and Linstead, *J.*, 1954, 3574.

[3] Bevington, *J.*, 1954, 3707.

[4] Goldschmidt and Renn, *Ber.*, 1922, **55**, 628.

[5] Lyons and Watson, *J. Polymer Sci.*, 1955, **18**, 141.

[6] Bevington, *Nature*, 1955, **175**, 477.

Similar experiments were done with diphenylpicrylhydrazine in place of the hydrazyl; the hydrazine interferes in the decomposition of the azo-compound. The results are summarized in Table 2.

TABLE 2.

Expt. no.	6	7	8	9
$(\text{:N}\cdot\text{CMe}_2\cdot\text{CN})_2$ (mg.)	6·5	12·1	6·7	3·5
$\text{NPh}_2\cdot\text{NHPc}$ (mg.)	31·1	73·8	41·5	21·1
C_6H_6 (c.c.)	1·6	2·75	1·5	1·0
Time at 60° (hr.)	4	6	24·5	78·5
$(\cdot\text{CMe}_2\cdot\text{CN})_2$ (mg.) : found	0·14	†	1·00	0·79
,, : expected in absence of $\text{NPh}_2\cdot\text{NHPc}$	0·15	0·54	1·49	1·29
Pr^iCN (mg.) : found	0·10	0·18	0·09	0·13
,, : expected in absence of $\text{NPh}_2\cdot\text{NHPc}$	0·13	0·54	0·50	0·22

As will be shown, it is possible to formulate a mechanism by which the hydrazine could interfere in the decomposition of the azo-compound and then by a subsequent reaction be regenerated. Expt. 10 was designed to see if the hydrazine is consumed during experiments such as those of Table 2. 4·2 mg. of unlabelled azo-compound and 27·6 mg. of [^{14}C]diphenylpicrylhydrazine in 1·05 c.c. of benzene were kept at 60° for 24½ hr. (the conditions resemble those of expt. 8); analysis for the hydrazine at the end of the reaction showed that 22·5 mg. remained and that therefore 5·1 mg. had been consumed.

If there is an exchange of hydrogen between diphenylpicrylhydrazine and the corresponding hydrazyl, isotope dilution analysis cannot be applied, without modification, to the determination of small quantities of the hydrazine formed from the labelled hydrazyl. To test this, small weights of labelled hydrazyl were mixed in solution with larger weights of the unlabelled hydrazine: small samples of pure diphenylpicrylhydrazine were then isolated and assayed. In all cases the hydrazine was radioactive and its specific activity was nearly that expected for complete exchange between the hydrazyl and the hydrazine (Table 3).

TABLE 3.

Expt. no.	11	12	13
[^{14}C]$\text{NPh}_2\cdot\text{NPc}$ (mg.)	5·55	5·28	14·20
[^{12}C]$\text{NPh}_2\cdot\text{NHPc}$ (mg.)	312·4	437·9	493·0
Solvent (c.c.)	5·0 (E)	2·0 (B)	10·0 (C)
Calc. c/m for complete exchange	989	683	1580
Obs. c/m for $\text{NPh}_2\cdot\text{NHPc}$	870	612	1540

E = ethyl acetate; B = benzene; C = chloroform.

In expt. 11, the solution of hydrazyl and hydrazine was kept at 60° for 23½ hr. in absence of air; in expt. 12 the air-free solution of the hydrazyl was kept at 60° for 40 hr. and then mixed with a solution of the hydrazine; in expt. 13 the solution of hydrazyl and hydrazine was kept at room temperature in the presence of air for 30 hr. before the hydrazine was recovered.

In spite of the rapid exchange, it is possible to use the labelled hydrazyl to see if the hydrazine is formed during the scavenging process. In expt. 14 and 15, 2-cyano-2-propyl radicals were generated from azo*iso*butyronitrile in the presence of excess of diphenylpicrylhydrazyl; isotope dilution analyses for the corresponding hydrazine were performed (Table 4).

TABLE 4.

Expt. no.	14	15	Expt. no.	14	15
$(\text{:N}\cdot\text{CMe}_2\cdot\text{CN})_2$ (mg.)	6·8	7·8	Time at 60° (hr.)	23·5	16·0
[^{14}C]$\text{NPh}_2\cdot\text{NPc}$ (mg.)	28·6	23·5	Carrier $\text{NPh}_2\cdot\text{NHPc}$ (mg.)	655·4	821·0
C_6H_6 (c.c.)	3·0	3·0	c/m for purified $\text{NPh}_2\cdot\text{NHPc}$	1050	665

Diphenylpicrylhydrazyl is an inhibitor for radical polymerizations.[7] In expt. 16, an air-free solution of azo*iso*butyronitrile in pure styrene (0·296 g./l. at 60°) was kept at 60°; the course of polymerization was followed dilatometrically. There was no induction period and the steady rate of polymerization was 1·30%/hr. In expt. 17, styrene containing the same concentration of azo*iso*butyronitrile but also 0·067 g. of diphenylpicrylhydrazyl per l. was treated similarly. For about 75 min. there was no observable polymerization; at that point the purple colour had almost completely disappeared and polymerization started. The conversion–time curves

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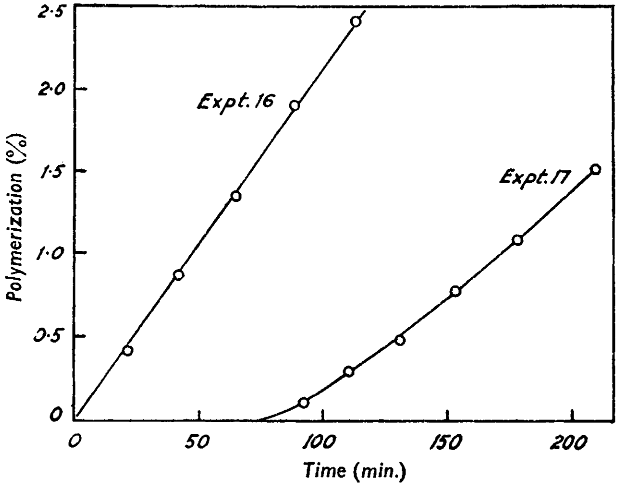
[7] Bartlett and Kwart, *J. Amer. Chem. Soc.*, 1950, **72**, 1051.

(Figure) show that the rate of polymerization in expt. 17 was considerably less than that in expt. 16.

In expt. 18, styrene containing 0·296 g. of azo*iso*butyronitrile and 0·090 g. of [^{14}C]diphenylpicrylhydrazyl (57,200 c/m) per l. was kept at 60° until the induction period was over and there had been about 2% of polymerization. The polymer was recovered by precipitation in methanol and purified by dissolution in benzene and reprecipitation in methanol. After drying, the polymer was buff in colour and possessed a counting rate of 43 c/m. This activity indicates that in the polymer one picryl group is combined for about 3000 molecules of monomeric styrene.



Polymerizations of styrene at 60°: *Expt.* 16, *diphenylpicrylhydrazyl absent*; *expt.* 17, *diphenylpicrylhydrazyl present.*

DISCUSSION

The results in Table 1 show that the products of the direct interaction of 2-cyano-2-propyl radicals are formed in appreciable quantities even although excess of diphenylpicrylhydrazyl is present in the solution. This indicates that a cage-effect may be operating or that part of the azo-compound decomposes by a mechanism not involving the liberation of free radicals. The apparent failure of the scavenger to capture all the radicals which seem to be generated in the solution is not confined to the hydrazyl, similar behaviour being observed if the azo-compound is decomposed in styrene.[8] It is perhaps significant that the yield of *iso*butyronitrile is depressed to a greater extent than that of tetramethylsuccinodinitrile. This may indicate that the azo-compound can decompose in two distinct ways; in the first, 2-cyano-2-propyl radicals are generated and in the absence of scavenger they interact by combination or disproportionation, but if sufficient scavenger is present they are all fixed; in the second type of decomposition, the dinitrile is formed but little *iso*butyronitrile is produced and this type of decomposition is unaffected by scavenger.

It has been suggested [9] that, to some extent, the following reactions occur :

$$\text{(i)}\quad \mathrm{CMe_2(CN)\cdot + NPh_2\cdot\underset{|}{N}\cdot C_6H_2(NO_2)_3 \longrightarrow CH_2{:}CMe\cdot CN + NPh_2\cdot NH\cdot C_6H_2(NO_2)_3}$$

$$\text{(ii)}\quad \mathrm{NPh_2\cdot NH\cdot C_6H_2(NO_2)_3 + CMe_2(CN)\cdot \longrightarrow NPh_2\cdot\underset{|}{N}\cdot C_6H_2(NO_2)_3 + CHMe_2\cdot CN}$$

This pair of reactions would allow for the regeneration of the hydrazyl and could account for the fact that the rate of production of radicals from azo*iso*butyronitrile is greater than the rate of removal of the hydrazyl, all the decomposed azo-compound being assumed to yield free radicals. If these reactions occur, significant quantities of *iso*butyronitrile should be formed when the azo-compound is decomposed in the presence of diphenylpicrylhydrazyl or its corresponding hydrazine, but expts. 5, 6, 7, 8, and 9 show conclusively

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[8] Bevington, *Trans. Faraday Soc.*, 1955, **51**, 1392.

[9] Hammond, Sen, and Boozer, *J. Amer. Chem. Soc.*, 1955, **77**, 3244.

that this is not the case; further, if reactions (i) and (ii) occur readily the diphenylpicrylhydrazine would not be consumed, but expt. 10 showed that this is not so.

The ready exchange between diphenylpicrylhydrazyl and the corresponding hydrazine complicates the analyses for the hydrazine. It can be shown however that a small amount of the hydrazine is formed by the reaction of the hydrazyl with 2-cyano-2-propyl radicals. For, in expt. 14, if there had been complete exchange between the whole of the labelled hydrazyl present originally and the carrier diphenylpicrylhydrazine, the counting rate for the hydrazine would have been 2400 c/m. In fact some of the hydrazyl was consumed but if all the consumed material had changed into the hydrazine and then the residual hydrazyl had undergone exchange with the carrier, the counting rate for the diphenylpicrylhydrazine would still have been 2400 c/m. That the activity of the hydrazine was considerably less than that calculated for complete exchange shows that, of the hydrazyl which was consumed, a considerable part was not converted into the hydrazine. If the activity in the diphenylpicrylhydrazine was due solely to exchange between the residual hydrazyl and the carrier hydrazine, *i.e.*, no hydrazine was formed from the hydrazyl during the reaction, the weight of unconsumed hydrazyl can be calculated from the weight of carrier and the counting rates of the original [^{14}C]hydrazyl and the isolated diphenylpicrylhydrazine. For expt. 14, the weight of unconsumed hydrazyl is calculated as 12·2 mg. and the weight consumed as 16·4. mg. From the results of Bawn and Mellish,[10] the weight of azo*iso*butyronitrile which decomposed to radicals which reacted with diphenylpicrylhydrazyl was 3·9 mg.; if one $CMe_2(CN)\cdot$ radical is equivalent to one hydrazyl molecule, this weight of azo-compound is equivalent to 18·7 mg. of the hydrazyl. The discrepancy between the two values for the weight of hydrazyl consumed suggests that some of the consumed material was converted into the hydrazine; it appears that about 12% of the consumed hydrazyl reacted in this way. The rate of consumption of the hydrazine (see expt. 10) is not sufficient to invalidate this conclusion. It is concluded that in expt. 15 about 8% of the consumed hydrazyl was converted into the hydrazine.

Diphenylpicrylhydrazyl is an inhibitor for the polymerization of styrene, and after the induction period the rate of polymerization is much less than that for a similar system free from the hydrazyl (cf. expts. 16 and 17). These observations show that during the induction period, when the hydrazyl is reacting with 2-cyano-2-propyl radicals, it is converted into a substance which reacts with radicals. This substance becomes incorporated in the polymer since the polymer is discoloured and possesses activity if labelled hydrazyl is used (expt. 18). An objection therefore to the use of diphenylpicrylhydrazyl as a radical scavenger in exact work is that the products of the scavenging action can themselves react with free radicals. This conclusion has also been reached by Bengough.[11]

If the induction period in expt. 17 is 75 min., 0·013 g. of the azo-compound decomposed to radicals which reacted with the hydrazyl; in this calculation 1 l. of solution is considered and the velocity constant for the first-order decomposition of the azo-compound is taken as $1{\cdot}0 \times 10^{-5}$ sec.$^{-1}$ from the work of Bawn and Mellish.[10] If one $CMe_2(CN)\cdot$ radical reacts with one molecule of the hydrazyl, 0·062 g. of the hydrazyl would have been consumed during the induction period. Actually 1 l. of the reaction mixture contained 0·067 g. of diphenylpicrylhydrazyl. The agreement between the two weights of the hydrazyl is good evidence that each molecule of the scavenger reacts with one radical during the induction period.

Diphenylpicrylhydrazine is a retarder for the sensitized polymerization of styrene.[12] A possible mechanism for the retarding action appears to be :

$$\text{(i)}\quad R{\cdot}CH_2{\cdot}CHPh{\cdot} + NPh_2{\cdot}NH{\cdot}C_6H_2(NO_2)_3 \longrightarrow R{\cdot}CH_2{\cdot}CH_2Ph + NPh_2{\cdot}\underset{|}{N}{\cdot}C_6H_2(NO_2)_3$$

$$\text{(ii)}\quad R{\cdot}CH_2{\cdot}CHPh{\cdot} + NPh_2{\cdot}\underset{|}{N}{\cdot}C_6H_2(NO_2)_3 \longrightarrow R{\cdot}CH{:}CHPh + NPh_2{\cdot}NH{\cdot}C_6H_2(NO_2)_3$$

where R = a polystyrene chain.

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[10] Bawn and Mellish, *Trans. Faraday Soc.*, 1951, **47**, 1216.
[11] Bengough, *Chem. and Ind.*, 1955, 599.
[12] Bevington, Ghanem, and Melville, unpublished work.

This is similar to a scheme discussed already;[9] according to it, the hydrazine would not become incorporated into the polymer but the use of labelled diphenylpicrylhydrazine has shown that the hydrazine does become incorporated in the polymer.[12]

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