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Decomposition of *m*-Nitrobenzenesulfonyl Peroxide in Several Solvents[1]

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Rates of decomposition of *m*-nitrobenzenesulfonyl peroxide in chloroform, nitrobenzene, chlorobenzene, and benzene were determined, and activation parameters were calculated. Products of decomposition in nitrobenzene were *m*-nitrophenyl *m*-nitrobenzenesulfonate and *m*-nitrobenzenesulfonic acid, whereas those in chloroform were *m*-nitrobenzenesulfonic acid, hexachloroethane, and phosgene (when air is present). Activation parameters and reaction products indicate that the reaction in chloroform involves homolytic cleavage of the O–O bond, whereas that in nitrobenzene involves electrophilic attack of the peroxide on aromatic nuclei. When sulfonyl-^{18}O labeled *m*-nitrobenzenesulfonyl peroxide was decomposed in benzene, about 35—36% of the label was found in the phenolic oxygen of *m*-nitrophenyl *m*-nitrobenzenesulfonate. This finding could be accounted for by a mechanism which involves a loose π-complex prior to the formation of a σ-complex.

The published chemistry of the bis(arenesulfonyl) peroxides is still very limited. In 1966 and 1970 Dannley and his co-workers[3] reported that the thermal decomposition of *m*-nitrobenzenesulfonyl peroxide in benzene, chlorobenzene, or toluene produced *m*-nitrobenzenesulfonic acid and the corresponding aryl *m*-nitrobenzenesulfonate. On the basis of the relative yields and orientations of the esters obtained from mixtures of benzene or toluene with chlorobenzene, they calculated partial rate factors and concluded that these products arose from electrophilic attack of the peroxide on aromatic compounds.

So far no good ways for production of sulfonyloxy radicals have been reported yet, and it appeared of interest to investigate the possibility of the homolytic decomposition of arenesulfonyl peroxides to produce arenesulfonyloxy radicals. Therefore, the decomposition of *m*-nitrobenzenesulfonyl peroxide (NBSP) has been investigated in chloroform and nitrobenzene; these solvents were chosen because they appeared least likely to receive electrophilic attack of the peroxide. Then the rate of decomposition in nitrobenzene was compared with those in chlorobenzene, benzene, and toluene. The results will be described in this paper.

Results and Discussion

Decomposition of NBSP in chloroform was followed by iodometric titration. The rates were of first order, and the first-order rate constants were 1.25, 4.88, and 9.90 $\times 10^{-5}$ sec^{-1} at 25.0, 35.0, and 40.0°C, respectively. From these values, E_a and $\Delta S^{\neq}$ were calculated to be 24.5 kcal/mol and 4.6 e.u., respectively. The products of

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[1] Organic Sulfur Compounds Part XXIV.

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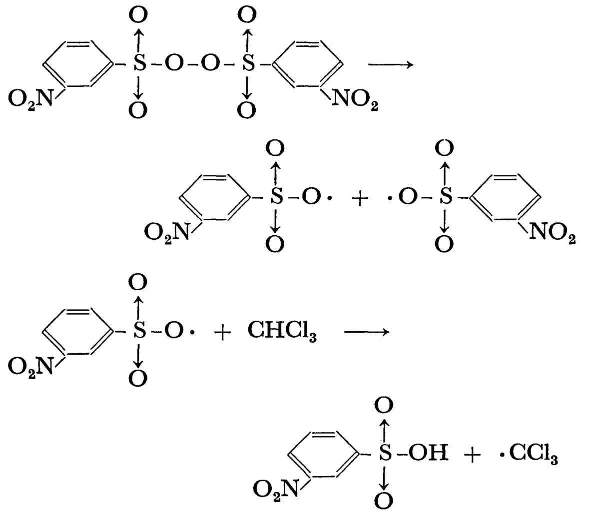
[3] R. L. Dannley and G. E. Corbett, *J. Org. Chem.*, **31**, 153 (1966); R. L. Dannley, J. E. Gagen, and O. J. Stewart, *ibid.*, **35**, 3076 (1970).

decomposition in chloroform were analyzed, and the results are shown in Table 1.

Table 1. Products of decomposition of NBSP in chloroform

Product	mol/mol of NBSP	
	Absence of O_2	Presence of O_2
m-$O_2NC_6H_4SO_3H$	1.79	2.06
C_2Cl_6	0.03	—
$COCl_2$	—	1.58

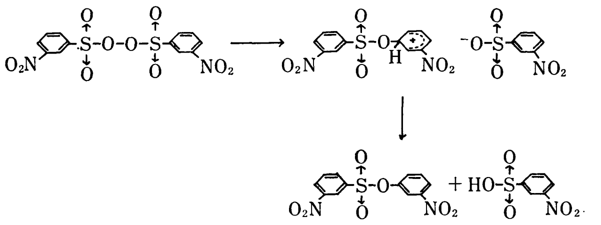
These results indicate that the decomposition of NBSP in chloroform involves homolytic cleavage of the O–O bond of NBSP, and the reaction steps are represented as follows.



$$2\cdot CCl_3 \longrightarrow Cl_3C\text{-}CCl_3$$

$$\cdot CCl_3 + O_2 \longrightarrow Cl_3C\text{-}O\text{-}O\cdot \longrightarrow\!\!\!\rightarrow Cl\text{-}\underset{\underset{O}{\|}}{C}\text{-}Cl$$

Then the decomposition of NBSP in nitrobenzene was investigated. The rates of decomposition in this solvent were also of first order in NBSP, and the rate constants were 1.40, 3.80, and 32.0×10^{-5} sec^{-1} at 20.0, 30.0, and 60.0°C, respectively. From these values E_a and $\Delta S^{\neq}$ were calculated to be 16.7 kcal/mol and -24 e.u., respectively. The products of decomposition in nitrobenzene are shown in Table 2. The products of decomposition and activation parameters indicate that the decomposition of NBSP in nitrobenzene is ionic, and the reaction probably proceeds as shown below.



Dannley and his co-workers did not determine the rate constants of decomposition of NBSP. Therefore it appeared of interest to determine the rate constants in various aromatic compounds. Kinetic studies were performed in chlorobenzene and benzene, and the results are shown in Table 3. Activation parameters and relative magnitude of rate constants are consistent with a mechanism which involves a nucleophilic attack of an aromatic compound on the peroxidic oxygen.

Table 2. Products of decomposition of NBSP in nitrobenzene

Product	mol/mol of NBSP
m-$O_2NC_6H_4SO_3H$	0.90
m-$O_2NC_6H_4SO_3C_6H_4$-NO_2-m	0.72

Table 3. Rate constants of decomposition NBSP in various Solvents

Solvent	Temp. (°C)	10^5k_1 (sec^{-1})	E_a (kcal/mol)	$\Delta S^{\neq}$ (e.u.)
$CHCl_3$	20.0	1.25	24.5	4.58
	35.0	4.88		
	40.0	9.90		
$C_6H_5NO_2$	20.0	1.40	16.7	−26.2
	30.0	3.80		
	60.0	32.0		
C_6H_5Cl	5.0	12.6	18.4	−13.2
	10.0	23.7		
	20.0	75.0		
C_6H_6	5.0	24.6	18.4	−12.0
	10.0	44.6		
	15.0	69.3		

Table 4. Comparison of rate constants and partial rate factors

Solvent	$10^5k_{10°}$ (sec^{-1})	k_X/k_H	Partial rate factor
$PhCH_3$	—	—	para, 73.8$^{b)}$
PhH	44.6	1.00	1.00
PhCl	23.7	0.53	para, 2.8
$PhNO_2$	0.500$^{a)}$	0.012	meta, 0.0336
$CHCl_3$	0.115$^{a)}$	—	—

a) Calculated by extrapolation of log k vs. $1/T$ plots.
b) Ref. 3.

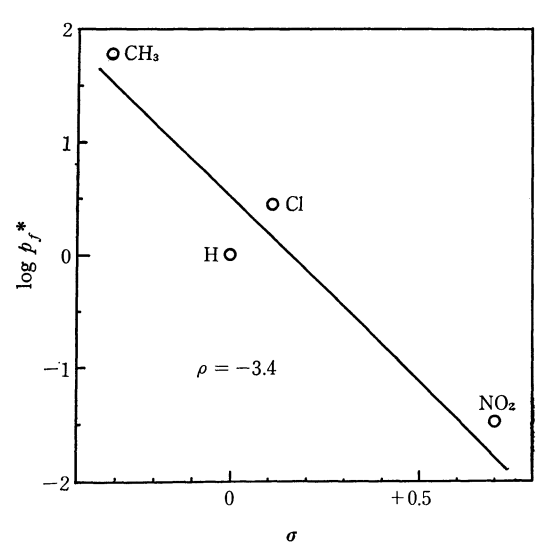
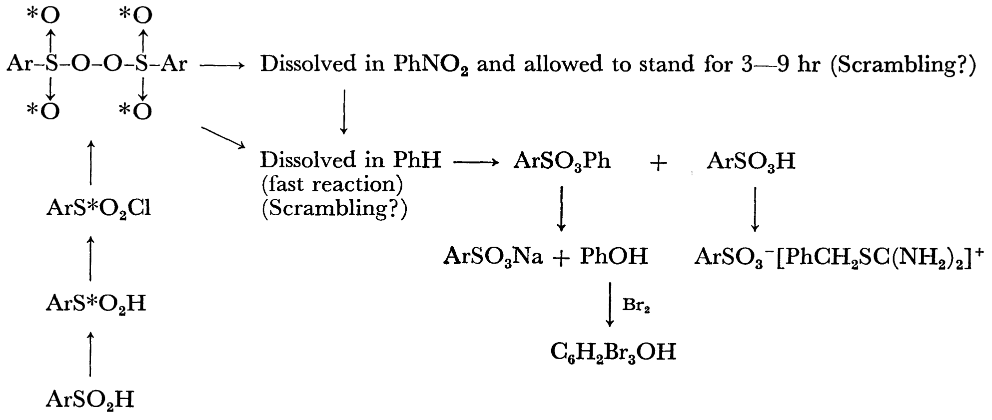


Fig. 1. Hammett plots for the decomposition of NBSP in aromatic solvents ($^*p_f$=partial rate fatctor)

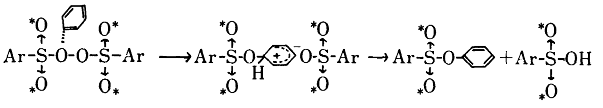


The rate constants at 10°C were compared and partial rate factors were calculated, which are shown in Table 4. Figure 1 is the Hammett plots of these partial rate factors against Hammett's σ values: ρ was found to be -3.4. The large negative ρ value indicates that the peroxidic oxygen is strongly electrophilic at the transition state, and the electron-releasing substituents on the aromatic solvents greatly facilitate the reaction.

In order to study the mechanism of the reaction between NBSP and aromatic compounds, sulfonyl-^{18}O labeled NBSP was prepared, and scrambling of the label was examined under various conditions. The experiments are summarized in the following scheme. The results are shown in Table 5.

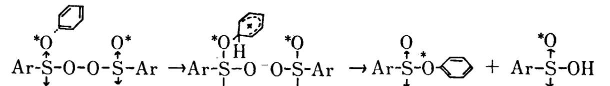
The following three cases are possible as the mechanisms of the reaction between NBSP and benzene.

A) Specific attack on peroxidic oxygen



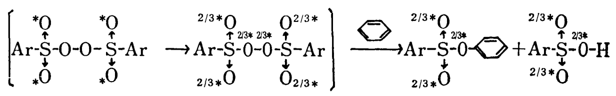
0% at phenolic oxygen

B) Specific attack on sulfonyl oxygen



100% at phenolic oxygen

C) Scrambling during preparation or standing, and then the reaction with benzene



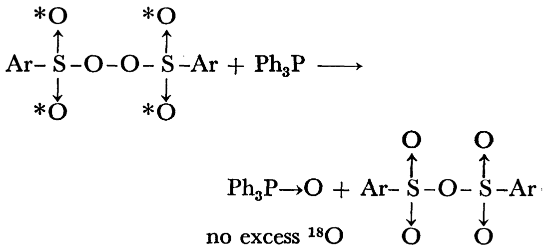
67% at phenolic oxygen

The possibility that the label was scrambled during the preparation of NBSP was excluded by use of the reaction of NBSP with triphenylphosphine. When the NBSP, prepared from *m*-nitrobenzenesulfonyl-^{18}O chloride with 1.08 excess ^{18}O atom %, was let to react with triphenylphosphine, the triphenylphosphine oxide produced was found to contain no excess oxygen-18.

TABLE 5. EXCESS OXYGEN-18 IN THE SULFONYL-LABELED NBSP AND THE PRODUCTS OF ITS REACTION WITH BENZENE

Expt No.	NBSP used	Treatment	*m*-$O_2NC_6H_4SO_3C_6H_5$ Excess ^{18}O%	*m*-$O_2NC_6H_4SO_3C_6H_5$ Excess ^{18}O% in SO_2	*m*-$O_2NC_6H_4SO_3^-$[$PhCH_2SC(NH_2)_2$]$^+$ Excess ^{18}O%	*m*-$O_2NC_6H_4SO_3^-$[$PhCH_2SC(NH_2)_2$]$^+$ Excess ^{18}O% in SO_2	C_6H_4BrOH Excess ^{18}O% (Y)	Y/X ×100
1	A	$PhNO_2$ 6 hr; then PhH, 18°C	0.404	1.01	0.417	1.04	0.37	35
2	B	PhH, 16°C	0.415	1.04			0.40	36
3	B	$PhNO_2$ 3 hr; then PhH, 16°C	0.405	1.00			0.40	36
4	B	$PhNO_2$ 9 hr; then PhH, 16°C	0.408	1.01			0.39	36

NBSP No.	*m*-$O_2NC_6H_4S^*O_2Cl$ Excess ^{18}O%	*m*-$O_2NC_6H_4S^*O_2Cl$ Excess ^{18}O% in SO_2	(*m*-$O_2NC_6H_4S^*O_2)_2O_2$ Excess ^{18}O%	(*m*-$O_2NC_6H_4S^*O_2)_2O_2$ Excess ^{18}O% in SO_2 (X)
A	0.520	1.04	0.420	1.05
B	0.540	1.08	0.440	1.08



$$\mathrm{Ar{-}}\overset{*\mathrm{O}}{\underset{*\mathrm{O}}{\overset{\uparrow}{\underset{\downarrow}{\mathrm{S}}}}}\mathrm{{-}O{-}O{-}}\overset{*\mathrm{O}}{\underset{*\mathrm{O}}{\overset{\uparrow}{\underset{\downarrow}{\mathrm{S}}}}}\mathrm{{-}Ar} + \mathrm{Ph_3P} \longrightarrow$$

$$\underset{\text{no excess }^{18}\mathrm{O}}{\mathrm{Ph_3P{\to}O}} + \mathrm{Ar{-}}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\overset{\uparrow}{\underset{\downarrow}{\mathrm{S}}}}}\mathrm{{-}O{-}}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\overset{\uparrow}{\underset{\downarrow}{\mathrm{S}}}}}\mathrm{{-}Ar}$$

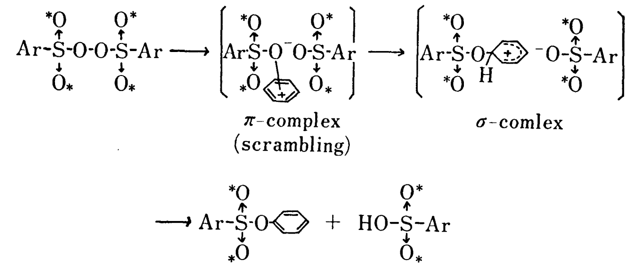
This finding establishes not only the non-occurrence of the scrambling of the label of NBSP during its synthesis but also the specific attack of triphenylphosphine upon the peroxidic oxygen of NBSP.

The data shown in Table 5 indicate that scrambling of the label does take place. When experiments 2, 3, and 4 are compared, it is clear that this scrambling does not take place during the long standing in nitrobenzene, but during the reaction with benzene. These findings indicate that Mechanism C) does not represent the reaction taking place.

The fact that the percentage of oxygen-18 excess found in the phenolic oxygen was neither 0% nor 100% shows that neither Mechanism A nor Mechanism B) alone can explain the reaction taking place. The figure 35—36% could be accounted for by an assumption that benzene molecules attack both peroxidic and sulfonyl oxygens. However, the possibility that the π-electrons of benzene nucleus attack negatively charged oxygen atoms of sulfonyl groups must be very small.

A more attractive mechanism for the reaction between NBSP and benzene is the following one.

D) Formation of a π-complex, and then a σ-complex.



Experimental

Materials. Nitrobenzene, chlorobenzene, benzene, toluene, and chloroform were purified by conventional procedures, and were distilled before use. Chloroform was used immediately after distillation in order to avoid contamination due to autooxidation.

m-Nitorobenzenesulfonyl peroxide was prepared from *m*-nitrobenzenesulfonyl chloride and hydrogen peroxide according to the method of Dannley and Corbett.[3] Yield, 12%, mp 112°C (dec.) (lit,[3] 112°C). The purity of the peroxide was determined by iodometric titration[4] to be 97.2%.

Determination of Rates of Reaction in Various Solvents. Into 100 m*l* of nitrobenzene in a flask placed in a bath of constant temperature, 0.625 g of NBSP (1.50 mmol) was added, and the flask was quickly shaken. At suitable intervals, certain amounts of the solution were withdrawn, and added to a flask containing crystals of potassium iodide. Then 10 m*l* of water was added, and the iodine liberated was titrated by a sodium thiosulfate solution.

Rates of reaction in other solvents were determined in a similar manner. Rates of reaction in chloroform were determined in sealed ampoules.

Products of Decomposition in Chloroform. *a) In a Degassed Chloroform*: A solution containing 0.941 g (2.33 mmol) of NBSP and 150 m*l* of chloroform was degassed, and placed in a bath of 40.0°C for 14 hr. The brown-colored solution was shaken with water. Evaporation of the aqueous extracts yielded 0.846 g (4.17 mmol) of *m*-nitrobenzenesulfonic acid, which was determined by converting it into *S*-benzylisothiuronium sulfonate. The chloroform solution was dried and evaporated. An oil obtained was analyzed by gas chromatography and it was found to contain 0.070 mmol of hexachloroethane.

b) In Chloroform Containing Air: A solution containing 0.260 mmol NBSP in 20 m*l* of chloroform was placed in a bath of 30.0°C for 29 hr in the presence of air. The solid *m*-nitrobenzenesulfonic acid which precipitated was decanted off, and aniline was added to the solution. Crystalline *N*, *N'*-diphenylurea formed weighed 0.0846 g (0.41 mmol); mp 233—234°C (decomp.). The same experiment was repeated for analysis of *m*-nitrobenzenesulfonic acid. After the decomposition the chloroform solution was washed with water. When the aqueous extracts were evaporated, 0.535 mmol of *m*-nitrobenzenesulfonic acid was obtained.

Products of Reaction in Nitrobenzene. In 20 m*l* of nitrobenzene 0.540 g (1.34 mmol) of NBSP was dissolved. A flask containing the solution was placed in a bath at 30.0°C for 2 days. Then the solution was washed with water several times. When the aqueous extracts were evaporated, *m*-nitrobenzenesulfonic acid was found, which was converted to its benzylisothiuronium salt (1.22 mmol).

When the nitrobenzene solution was evaporated, brownish solids remained, which was recrystallized in hexane and found to be *m*-nitrophenyl *m*-nitrobenzenesulfonate, mp 98—103°C. The ester was refluxed in 10 m*l* of 0.3N sodium hydroxide solution for 5 days, and the nitrophenol produced was methylated by use of dimethyl sulfate. When the nitroanisole obtained was analyzed by gas chromatography, only one peak was observed which corresponded to that of *m*-nitroanisole.

Preparation of Sulfonyl-^{18}O labeled m-*Nitrobenzenesulfonyl Peroxide.* In 41.5 m*l* of $H_2{}^{18}O$ (1.53 excess-^{18}O atom %) 23.5 g of *m*-nitrobenzenesulfinic acid was dissolved and the solution was heated at 90°C for 45 min after which the exchange of oxygen was almost complete. The sulfinic acid was converted to its sodium salt, which was treated with chlorine for 25 min and converted to *m*-nitrobenzenesulfonyl chloride. Crude crystals obtained (20 g) were recrystallized in hexane; yield, 10 g, mp 61—63°C. Its excess oxygen-18% was analyzed by mass spectrometry, and the results are shown in Table 5.

By using sulfonyl-^{18}O labeled *m*-nitrobenzenesulfonyl chloride and 30% hydrogen peroxide, sulfonyl-^{18}O labeled NBSP was prepared according to the method of Dannley and Corbett.[3]

Reaction of Sulfonyl-^{18}O labeled NBSP with Aromatic Solvents. As a representative case the experimental procedure used for Experiment 2 in Table 5 will be described. In 140 m*l* of purified nitrobenzene 2.002 g of sulfonyl-^{18}O labeled NBSP was dissolved, and the solution was stirred for 6 hr under a nitrogen atmosphere at 18°C. Then 300 m*l* of purified benzene was added, and the mixture was allowed to stand for 48 hr under a nitrogen atmosphere.

The reaction mixture was extracted with water. The *m*-nitrobenzenesulfonic acid in the aqueous extracts were con-

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[4] R. N. Haszeldine, R. B. Heslop, and J. W. Lethbridge, *J. Chem. Soc.*, **1964**, 4902.

verted to its *S*-benzylisothiuronium salt, which amounted to 1.405 g (76.5%). Crude crystals were recrystallized in ethanol-water, and the purified crystals (0.10 g) melting at 140.0—142.3°C were subjected to the mass-spectrometric analysis.

The aromatic hydrocarbon layer was dried over anhydrous magnesium sulfate, and the solvents were distilled under reduced pressure. The residue was chromatographed by a column containing 50 g of Florisil, and 1.008 g of phenyl *m*-nitrobenzenesulfonate was obtained from fractions eluted by hexane-benzene; yield, 72.4%. Crude crystals were recrystallized in methanol, and the purified crystals melting at 91—91.5°C were subjected to the mass-spectrometric analysis.

In order to separate the phenolic oxygen from the sulfonyl oxygen the ester was hydrolyzed. In 5 m*l* of a 0.3N sodium hydroxide solution in 70% dioxane-30% water, 0.252 g of phenyl *m*-nitrobenzenesulfonate was added, and the mixture was heated at 60°C in an ampoule for 7 days. After the solution was acidified by hydrochloric acid, a Br_2-KBr solution was added and white precipitates formed were washed with a sodium hydrogen sulfite solution and then with water. After drying, crude crystals of 2,4,6-tribromophenol weighed 0.335 g. They were purified by sublimation at 140°C under reduced pressure, and the purified crystals weighed 0.227 g (75.7%); mp 88.5—91.0°C.

The possibility that the oxygens of phenyl *m*-nitrobenzenesulfonate are scrambled during its hydrolysis can be excluded on the basis of the findings of Bunton and Frei, who studied the alkaline hydrolysis of phenyl *p*-toluenesulfonate in dioxane-water.[5] They showed that no C–O bonds were cleaved during hydrolysis and the S–O bond fission took place exclusively.

Reaction of Sulfonyl-^{18}O labeled NBSP with Triphenylphosphine. A solution of 2.0 g of triphenylphosphine in 20 m*l* of dichloromethane was slowly added to a stirred solution of 0.70 g of sulfonyl-^{18}O labeled NBSP in 50 m*l* of dichloromethane at room temperature. The reaction mixture was extracted with water, and the aqueous extracts were evaporated. Crystals of *m*-nitrobenzenesulfonic acid obtained were converted to its *S*-benzylisothiuronium salt, which amounted to 0.683 g. The dichloromethane solution was evaporated and the residue was washed with ether. The ether-insoluble solids were dissolved in benzene, and the solution was filtered in order to remove benzene-insoluble solids. When the benzene filtrate was evaporated, 0.480 g of white solids of triphenylphosphine oxide were obtained. They were recrystallized from ether, and purified crystals were subjected to the mass-spectrometric analysis.

Oxygen-18 Analysis. The oxygen-18 analyses were carried out according to the method of Rittenberg and Ponticorvo.[6] Each sample was pyrolyzed in the presence of mercuric chloride and mercuric cyanide at 400°C for 4 hr, and the oxygen-18 atom% of the carbon dioxide produced was determined by use of a Hitachi RMU-6D type mass spectrometer.

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[5] C. A. Bunton and Y. F. Frei, *J. Chem. Soc.*, **1951**, 1872.

[6] D. Rittenberg and L. Ponticorvo, *Int. J. Appl. Radiat. Isotopes*, **1**, 208 (1956).