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A Comparison of the Radiation-Induced Reaction with Photochemical and Thermal Reactions. I. The Radiation-Induced Isomerization of *o*-Nitrobenzaldehyde in the Solid State

By Akira SUGIMORI, Kōichi NAKATA and Hachiro HIRAI

Department of Chemistry, Faculty of Science and Technology, Sophia University, Chiyoda-ku, Tokyo

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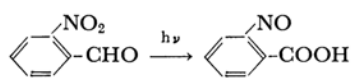
The radiation-induced reaction of *o*-nitrobenzaldehyde in the solid state was investigated. Isomerization to *o*-nitrosobenzoic acid preferentially took place. This suggests that the γ-ray irradiation produces effectively the excited *o*-nitrobenzaldehyde which is identical with that produced by ultraviolet irradiation.

The radiation-induced reaction has often been compared with the photochemical reaction using rather simple compounds.[1-5] However, only a few studies have been carried out with complex compounds.

The photochemical reaction of *o*-nitrobenzaldehyde was studied by Ciamician and Silber,[6] and by Leighton and Lucy.[7] These studies showed that the following isomerization proceeds intramolecularly both in solid state and in a solution, with no side reaction.



(1)

This system is considered to be suitable for the comparison of radiation-induced reaction with the photochemical reaction from the following reasons. First, little kinetical consideration is needed for the interpretation of the reaction because of the intramolecular rearrangement. Secondly, the photochemical reaction of *o*-nitrobenzaldehyde has already been elucidated, not only with a solution but also with the solid state. Direct excitation by ionizing radiation can not be expected with a solution.

Results and Discussion

The results of the analysis of the gaseous products from the γ-ray-irradiated solid *o*-nitrobenzaldehyde are listed in Table I.

Table I. Gaseous products from the γ-ray irradiated *o*-nitrobenzaldehyde

i) Condition of irradiation
Dose Rate : 3.3×10^{19} eV./g.hr.
Total Dose : 2.0×10^{22} eV./g.

ii) G(total gaseous products)$=0.2$

Component	
CO_2	82%
CO	16%
H_2	2%
NO_2, NO, N_2O	—

No oxides of nitrogen (N_2O, NO and NO_2) were observed to be formed. The evolved gas consisted of carbon dioxide, carbon monoxide, and a small amount of hydrogen. However, the yields of the gaseous products were small and the G value for the total gaseous products was found to be 0.2.

In contrast with the small G value of the radiolytic decomposition, the radiation-induced isomerization of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid proceeds in a highly efficient manner. The results of the analyses of the γ-ray-irradiated *o*-nitrobenzaldehyde are shown in Table II.

Table II. The analysis of the γ-ray irradiated *o*-nitrobenzaldehyde

Run	1	2	3
Absorbed radiation dose (eV./g.)	5.0×10^{21}	2.1×10^{22}	2.4×10^{22}
Purity of the sample (%)	97.7	97.7	97.7
Formed *o*-nitroso-benzoic acid (%)	6.6	34.1	37.6
Unreacted *o*-nitro-benzaldehyde (%)	91.0	62.3	56.8
Side reaction (%)	0.1	1.3	3.3

1) G. J. Mains and A. S. Newton, *J. Phys. Chem.*, **65**, 212 (1961).
2) H. A. Dewhurst, ibid., **63**, 813 (1959).
3) R. B. Cundall and P. A. Griffith, *Discussions Faraday Soc.*, **36**, 111 (1963).
4) M. Katayama, J. C. Whitmer and C. N. Trumbore, *J. Am. Chem. Soc.*, **84**, 4025 (1962).
5) A. Scala and P. Ausloos, *J. Phys. Chem.*, **70**, 260 (1966).
6) G. Ciamician and P. Silber, *Ber.*, **34**, 2040 (1901).
7) P. A. Leighton and F. A. Lucy, *J. Chem. Phys.*, **2**, 760 (1934).

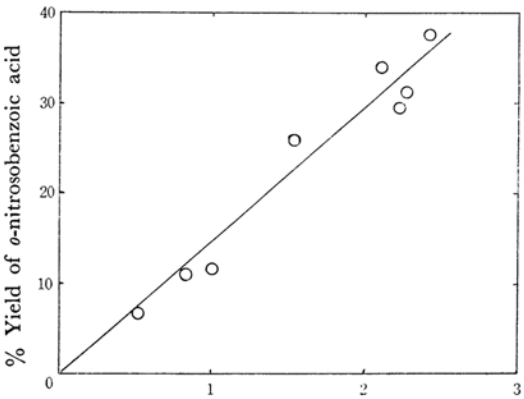


Fig. 1. Relation between the yield of *o*-nitrosobenzoic acid and the absorbed radiation dose.

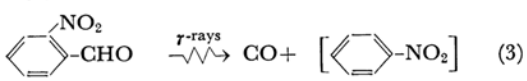
The formation of *o*-nitosobenzoic acid is plotted against the absorbed radiation dose in Fig. 1.

As is shown in Table II, the formation of *o*-nitrosobenzoic acid can explain more than 90% of the reaction of *o*-nitrobenzaldehyde. At a rather high dose of irradiation, where 35.4% of the original *o*-nitrobenzaldehyde was consumed (Run 2 in Table II), the side reaction was only 3.8% of the isomerization.

A linear relationship was observed between the yield of *o*-nitrosobenzoic acid and the absorbed radiation dose in the range where the conversion was below 40%. The *G* value for the *o*-nitrosobenzoic acid formed is found from Fig. 1 to be 5.8.

Since the *G* value of the main reaction is 5.8, the *G* value of the side reaction can be estimated as 0.2—0.5. Most of the side reaction may be explained by the reaction that gives rise to the formation of gaseous products, because the *G* value for the gaseous products is nearly equal to the *G* value for the side reaction. Judging from the composition of the gaseous products, the side reactions may be:

(2)



(3)

The reactions to give oxides of nitrogen and hydrogen are negligible.

Since carbon dioxide is considered to come from the secondary decomposition of the initially-produced *o*-nitrosobenzoic acid, the only side reaction at the initial stage is the decarbonylation reaction (reaction 3). Reaction 3 plays a minor part in the side reactions (it comprises 1/6 of the total side reactions), so the side reactions at the initial stage may be smaller than as evaluated above.

These facts indicate that the γ-ray irradiation gives rise preferentially to the isomerization of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid.

It can be said that the identity of the reaction in such a special case as the isomerization of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid indicates the identity of the reaction mechanism and the identity of the excited molecules included in the reaction. In the radiation-induced reaction of *o*-nitrobenzaldehyde, the same excitation as that in photochemical reaction is preferentially produced. Analogous results have been obtained in the radiolysis of oxalato metal complexes.[8] These compounds have an efficient reaction path for the absorption of light (the supply of relatively low energy), and the radiation-induced reaction occurs selectively and with a high effciency through this reaction path.

As to the yields of the isomerization by light and by ionizing radiation, the following explanation may hold.

Leighton and Lucy showed that the quantum yield of the isomerization is 0.5 for ultraviolet light of 3660 Å (3.4 eV.), 3130 Å (4.0 eV.), and 2537 Å (4.4 eV.).[7] Therefore, the supply of at least about 7 eV. of light energy is necessary for each *o*-nitrosobenzoic acid molecule. On the other hand, the *G* value of the isomerization in γ-ray irradiation was 5.8. This means that 17 eV. of radiation energy is required for the production of each *o*-nitrosobenzoic acid molecule. This suggests that most of the radiation energy absorbed was lost in the form of heat without bringing the molecules of *o*-nitrobenzaldehyde to excitation.

Experimental

Materials.—Commercially-available *o*-nitrobenzaldehyde (guaranteed reagent-grade; Tokyo Kasei Co.) was used without further purification. The purity of the sample, which was determined by the gravimetric analysis to be 2, 4-dinitrophenylhydrazone, was 97.7%. *o*-Nitrosobenzoic acid was produced by the ultraviolet irradiation of *o*-nitrobenzaldehyde in a benzene solution.[6]

Gamma-Irradiation.—One to two grams of *o*-nitrobenzaldehyde were sealed in a tube with a break-off seal in a vacuum. The samples were irradiated by Co-60 γ-rays in the irradiation facility, equipped with a Co-60 source of 16000 curies, at the Japan Atomic Energy Research Institute.

Gaseous Products.—The break-off seal of the tube containing the γ-ray-irradiated *o*-nitrobenzaldehyde was cut in the vacuum system, the volume of which had been measured in advance. The pressure increase in the vacuum system permitted us to determine the quantity of gas evolved. Some of the gaseous products were analyzed by the mass spectrometric method. A CEC Model 103C mass spectrometer was used. The quantity of CO_2 was estimated from the peak at $m/e=44$. The ratio of CO to CO_2 was evaluated from the peaks.

8) A. Sugimori, This Bulletin, **38**, 2583 (1966).

at $m/e=12$ and 44. The hydrogen content was estimated from the peak at $m/e=2$. The lack of the peak at $m/e=30$ indicates the absence of N_2O, NO and NO_2.[9]

The Determination of *O*-Nitrosobenzoic Acid.—Gamma ray-irradiated *o*-nitrobenzaldehyde was treated three times with each 5-ml. portion of benzene, and the benzene-insoluble substance was collected on a sintered glass filter. It was dried at 80°C and weighed. The substance was identified as *o*-nitrosobenzoic acid from its infrared spectra (Fig. 2).

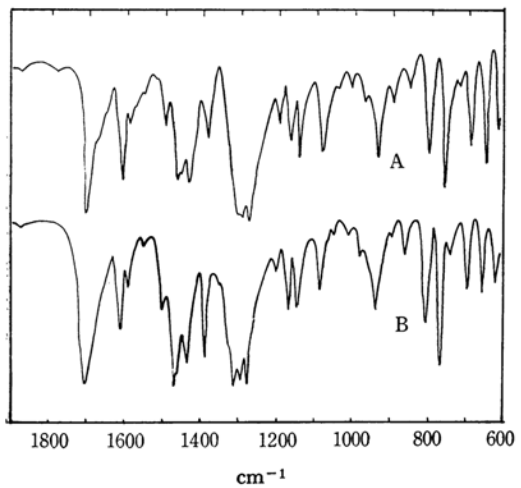


Fig. 2. Infrared spectra of *o*-nitrosobenzoic acid (A) and the benzene-insoluble substance from γ-irradiated *o*-nitrobenzaldehyde (8.0×10^{21} eV./g.) (B). Nujol mull method.

The Determination of the Residual *O*-Nitrobenzaldehyde.—Benzene-soluble portions of the γ-ray-irradiated *o*-nitrobenzaldehyde were collected. The solvent was evaporated by leaving the solution to stand at room temperature for several days in the dark in order to protect it from photo-isomerization. Figure 3 shows the infrared spectra of the benzene-soluble substance from the *o*-nitrobenzaldehyde irradiated at 8.1×10^{21} eV./g. of the absorbed radiation dose (10.7% of conversion).

All of the bands except that at 1785 cm^{-1} can be accounted for by *o*-nitrobenzaldehyde.

All the infrared spectra of γ-ray-irradiated *o*-nitrobenzaldehyde (Fig. 4) can be explained by the superposition of those of *o*-nitrobenzaldehyde and *o*-nitrosobenzoic acid, except for the weak band at 1785 cm^{-1}, which probably came from side reaction.

The quantitative analysis of *o*-nitrobenzaldehyde was carried out by gravimetric analysis in the form of 2, 4-dinitrophenylhydrazone. The residue, after the evaporation of benzene, was dissolved in ethanol and treated with an acidic solution of 2, 4-dinitrophenylhydrazine.

9) "Catalog of Mass Spectral Data," American Petroleum Institute Res. Project No. 44, Serial No. 96, 1218 and 95.

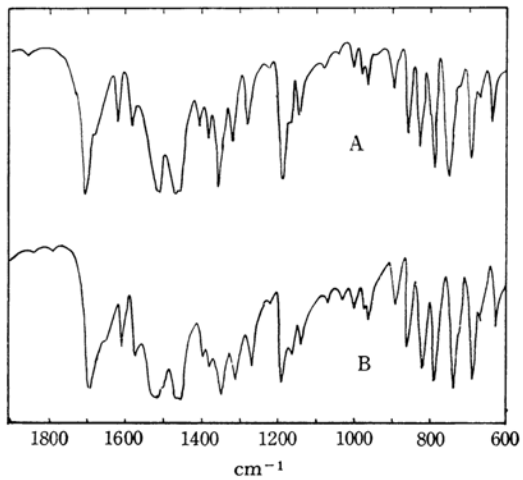


Fig. 3. Infrared spectra of *o*-nitrobenzaldehyde (A) and the benzene-soluble substance from γ-irradiated *o*-nitrobenzaldehyde (8.1×10^{21} eV./g.) (B). Nujol mull method.

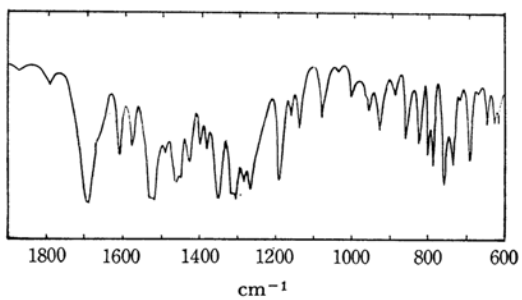


Fig. 4. Infrared spectra of γ-irradiated *o*-nitrobenzaldehyde (2.1×10^{22} eV./g.). Nujol mull method.

The 2, 4-dinitrophenylhydrazone thus formed was then collected on a sintered glass filter and weighed.

Annealing.—It was shown that the prolonged standing of the irradiated sample caused a secondary reaction of the initial product. A sample which had been stored for 8 months after a 1.5×10^{22} eV./g. irradiation showed a higher yield of the side reaction (31% against the isomerization), while the samples which were analyzed soon after irradiation gave side reactions of below 10% as is shown in Table II. The infrared absorption at 1785 cm^{-1} cited above is due to this side reaction.

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