Photomethylation of Inorganic Mercury by Aliphatic α-Amino-acids

By K. HAYASHI, S. KAWAI, T. OHNO, and Y. MAKI*
(*Gifu College of Pharmacy*, 6-1, *Higashi*-5-*Chome*, *Mitahora*, *Gifu*, 502, *Japan*)

Summary Photolysis of aliphatic α-amino-acids in the presence of mercury(II) chloride resulted in the formation of methylmercury arising from apparent fragmentation of the alkyl residue of the α-amino-acids.

PHOTOCHEMICAL alkylation of inorganic mercury by using aliphatic carboxylic acids is well documented.[1] Recently, a detailed study[2] on the photolysis of aqueous acetic acid containing inorganic mercury has suggested one of the pathways leading to the formation of highly neurotoxic methylmercury in the natural environment.

We now report that photolysis of aliphatic α-amino-acids in the presence of inorganic mercury also results in the formation of methylmercury.

A significant feature of the present observation is the almost exclusive formation of methylmercury regardless of alkyl residues in the α-amino-acids used. Thus, the present results suggest that aliphatic α-amino-acids are a possible source for the photochemical formation of methylmercury in nature, and provide a novel example of photolysis of simple aliphatic α-amino-acids[3] in the presence of a metal ion.

$$\mathrm{RCH(NH_2)CO_2H} \xrightarrow[\mathrm{HgCl_2}]{h\nu} \mathrm{MeHgCl}$$

α-Amino-acid	MeHgCl produced[a] /μg
R = Me	443
$\mathrm{Pr^i}$	84
$\mathrm{Bu^i}$	157
$\mathrm{Bu^s}$	41

[a] From 2·5 mmol of $HgCl_2$ and 7·5 mmol of amino-acid

SCHEME

Solutions of DL-alanine, DL-valine, DL-leucine, or DL-isoleucine (7·5 mmol) in water (300 ml) containing $HgCl_2$ (2·5 mmol) were irradiated in a quartz vessel by an 8 W low-pressure mercury arc lamp (253·7 nm) for 4 h. The mixtures were then acidified with hydrochloric acid, and the alkylmercury(II) chlorides produced were analysed quantitatively by g.l.c.

Although DL-leucine gave an underdetermined organomercury compound as a minor product in addition to methylmercury, in other cases only the formation of methylmercury was observed, in amounts which are shown in the Scheme.

Other alkylmercury-compounds were not detected even after irradiation for shorter periods. Methylmercury was not formed in the photolysis of ethyl-, n-propyl-, or isopropyl-mercury(II) chloride under analogous condition. Analysis of methylmercury after various irradiation times indicated partial degradation of the initially produced methylmercury during irradiation. Photolysis of glycine did not give alkylmercury compounds.

The use of a 20W blacklight lamp (300—400 nm) as a light source resulted in the formation of methylmercury in much lower yield after irradiation for 150 h. This slow formation of methylmercury in the blacklight-lamp irradiation, however, was significantly accelerated by addition of Cu^{2+} ion which has a better chelating ability, and the presence of which could increase the efficiency of light absorption. This suggests that many factors should be taken into consideration in the formation of methylmercury in natural sunlight.

Although the detailed mechanism is not clear at present, the photomethylation of inorganic mercury by aliphatic α-amino-acids could involve the reaction of a mercury(II) ion with a methyl radical formed ultimately *via* photofragmentation of aliphatic α-amino-acids. The present photoreaction is of interest in connection with photofragmentation of the alkyl residue in simple aliphatic carboxylic acids in the presence of *o*-aminobenzenethiol which has been observed previously.[4]

(*Received*, 18*th November* 1976; *Com.* 1271.)

---

[1] *E.g.* Y. A. Ol'dekop, N. A. Maier, and V. I. Gesel'berg, *Sbornik Nauch Rabot, Akad. Nauk Belorus, S.S.R., Inst, Fiz, Org. Khim,* 1960, **8**, 37 (*Chem. Abs.*, 1962, **56**, 3051).

[2] H. Akagi, Y. Fujita, and E. Takabatake, *Chemistry Letters*, 1973, 1, and earlier papers.

[3] J. P. Greenstein and M. Winitz, 'Chemistry of the Amino Acids, Vol. 1,' Wiley, New York, London, 1961, p. 683.

[4] Y. Maki and M. Suzuki, *Chem. Comm.*, 1971, 177.