

Positron Decay in Halogen Compounds

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The decay of positrons has been investigated in the halogen derivatives of benzene, both at room temperature and at -100°C , and in a number of halogen compounds. A lifetime of the order of 4×10^{-10} sec is found in all the investigated compounds but fluorobenzene, and suggests the presence of a positron-halogen bound state; a search for the excited levels of such a bound state, whose decay features were predicted by Goldansky and co-workers, was inconclusive.

1. INTRODUCTION

THOUGH positronium formation is considered impossible in alkali halides on the basis of general considerations,¹ recent results²⁻⁴ showed that the decay features of positrons in such materials are not consistent with the hypothesis of free annihilation: In particular Bisi *et al.*³ showed that, besides the usual short lifetime, another lifetime is displayed by all the alkali halides and its value ranges between 4 and 7×10^{-10} sec, depending on the halogen and on the density of the material.

These long lifetimes were explained in terms of positron-halogen bound states, first predicted by Simons.^{5,6} Detailed calculations in this direction were carried out by Goldansky *et al.*⁷ who took into explicit consideration the case of lithium hydride. It is felt that the conclusions which were reached might suggest some general features and the order of magnitude of the decay parameters of positrons in alkali halides. The main conclusion was that the complex decay observed² in LiH could be explained in terms of decay of both ground level and excited levels of the Li^+H^-e^+ system, competition arising between annihilation and radiative decay as far as the excited levels are concerned. In a recent paper⁸ Goldansky *et al.* also took into consideration some mechanisms involving lattice deformation and defects which, in alkali halides, might be responsible for the observed lifetime.

It appears reasonable to suppose that the formation of positron-halogen bound states is not an exclusive peculiarity of ionic compounds. In particular many data are available⁹ concerning the positron decay in the halogen derivatives of benzene^{9,10}; but while the ener-

getics of positronium formation¹¹ and other features like positronium quenching^{10,12} were considered rather carefully, no experimental investigation was detailed enough to allow conclusions as far as positron capture by halogen atoms is concerned. No data are available on the possible existence of lifetimes of the order of $4-7 \times 10^{-10}$ sec like those observed for alkali halides and attributed to positron-halogen bound states.

It seemed convenient therefore to investigate the decay features of positrons in a number of halogen compounds, with the aim of clarifying the question of whether a decay mechanism exists which is associated with the formation of these bound states.

2. EXPERIMENTAL PROCEDURE

The time analyzer used for the measurements to be discussed was the one described by Cottini *et al.*,¹³ its characteristics having been improved with respect to those reported therein. In particular, the time resolution, defined by the full width at half-height of a prompt coincidence curve, was better than 10^{-9} sec. The detectors were two RCA 6342 A photomultipliers, optically coupled to NE 102 plastic scintillators ($1\frac{1}{2}$ in. thick, $1\frac{1}{2}$ in. in diameter).

A $30\text{-}\mu\text{Ci}$ positron source was prepared by evaporation of Na^{22}Cl hydrochloric solution between two thin mica foils (4 mg/cm^2). The source was then sealed and placed within a metallic container, into which the liquid specimen to be investigated was introduced. Solid specimens, in the shape of conveniently pressed cylinders, could be put into the same container, so that the geometry was identical in each case.

In order to evaluate the influence of positron absorption by mica, the delay spectrum obtained with a Teflon specimen within the mentioned container was compared with the delay spectrum from the same specimen onto which Na^{22} had been directly deposited. The measured intensity of the τ_2 lifetime (I_2) which resulted was reduced by about 5%, and the I_2 values quoted in the next section were therefore the experimental ones multiplied by 1.05.

A similar measurement was carried out with alumi-

¹ R. A. Ferrel, Rev. Mod. Phys. **28**, 308 (1956).

² A. Bisi, A. Fiorentini, and L. Zappa, Phys. Rev. **131**, 1023 (1963).

³ A. Bisi, A. Fiorentini, and L. Zappa, Phys. Rev. **134**, 328 (1964).

⁴ A. Gainotti, E. Germagnoli, G. Schianchi, and L. Zecchina, Phys. Letters **13**, 9 (1964).

⁵ L. Simons, Phys. Rev. **90**, 165 (1953).

⁶ L. Simons, Soc. Sci. Fennica Commentationes Phys. Math. **14**, 9 (1949).

⁷ V. I. Goldansky, A. V. Ivanova, and E. P. Prokopiev, Zh. Eksperim. i Teor. Fiz. **47**, 659 (1964) [English transl.: Soviet Phys.—JETP **20**, 440 (1965)].

⁸ V. I. Goldansky and E. P. Prokopiev, Fiz. Tverd. Tela **6**, 3301 (1964) [English transl.: Soviet Phys.—Solid State **6**, 2641 (1965)].

⁹ C. R. Hatcher, W. E. Millet, and L. Brown, Phys. Rev. **111**, 12 (1958).

¹⁰ V. I. Goldansky, T. A. Solonyenko, and V. P. Shantarovich, Dokl. Akad. Nauk SSSR **151**, 608 (1963).

¹¹ C. R. Hatcher, J. Chem. Phys. **35**, 2206 (1961).

¹² J. H. Ormrod and B. G. Hogg, J. Chem. Phys. **34**, 624 (1961).

¹³ C. Cottini, E. Gatti, and F. Vaghi, in *L'Electronique Nucléaire, Comptes Rendus du Colloque Internationale, Paris, 1958* (International Atomic Energy Agency, Vienna, 1959), Vol. 1, p. 177.

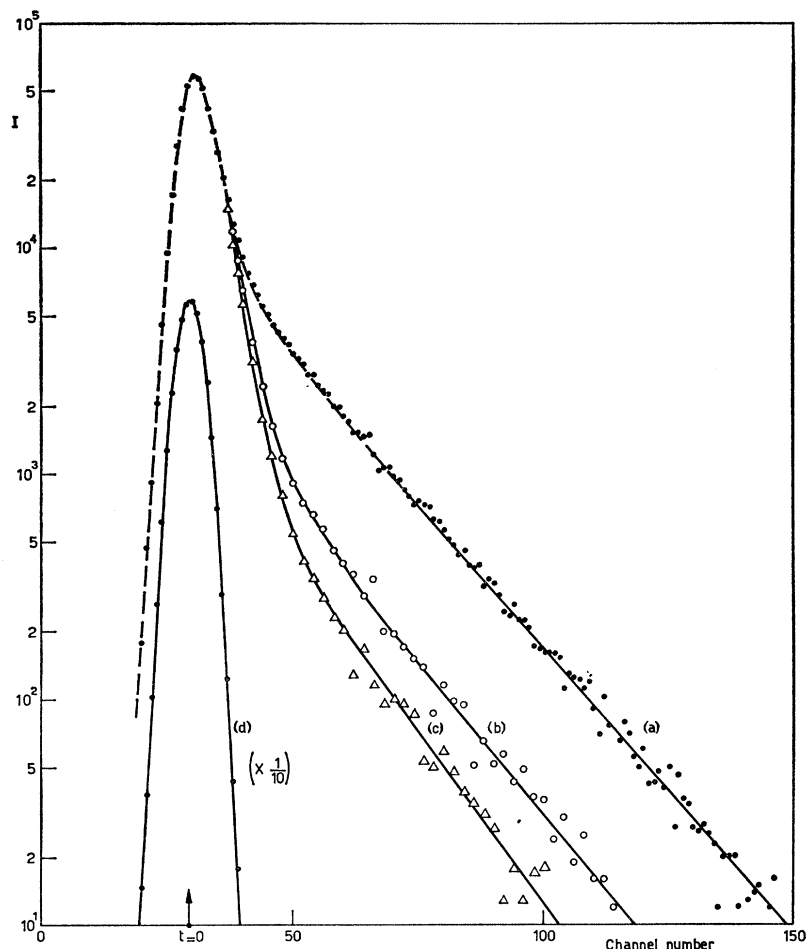


FIG. 1. Typical delay curves. 1 channel = 1.41×10^{-10} sec. (a)-benzene. (b)-chlorobenzene. (c)-bromobenzene. (d)-prompt coincidence curve.

num in order to observe possible effects of the source on the short lifetime, but no effect was found.

The best fit of the experimental delay curves was obtained with the help of a ELEA 6001 Olivetti digital computer. The analysis of the data was performed under the hypothesis that two lifetimes, τ_1 and τ_2 , were present. It will be seen from the next sections that τ_1 is of the order of 4×10^{-10} sec, the only exceptions being benzene and fluorobenzene at room temperature, for which materials τ_1 is about 2×10^{-10} sec. This is the usual order of magnitude resulting from free-positron decay and singlet annihilation of positronium. The analysis does not rule out the possibility that such a fast decay is present in all the investigated materials, but does lead to the conclusion that the fastest component in no case involves more than 20% of the decays.

3. EXPERIMENTAL RESULTS: BENZENE AND HALOGEN DERIVATIVES OF BENZENE; BENZENE-IODOBENZENE MIXTURES

The decay features of positrons in the halogen derivatives of benzene, at room temperature, were reinvestigated in a first run of measurements. The ex-

perimental results are collected in Table I, and a few typical delay curves are shown in Fig. 1, together with a prompt curve, which was obtained with a Co^{60} source and with the same amplitude requirements which were adopted for the Na^{22} positron source.

A preliminary conclusion which can be drawn from these data is that positronium formation is not probable

TABLE I. Experimental data on halogen derivatives of benzene and benzene-iodobenzene mixtures.

Compound or mixture	$\tau_1 \times 10^{10}$ (sec)	$\tau_2 \times 10^9$ (sec)	I_2 (%)
C_6H_6	2.0 ± 0.6	2.39 ± 0.05	34.8
$\text{C}_6\text{H}_5\text{F}$	1.9	2.48	19.4
$\text{C}_6\text{H}_5\text{Cl}$	4.4	2.36	8.4
$\text{C}_6\text{H}_5\text{Br}$	4.1	2.06	5.6
$\text{C}_6\text{H}_5\text{I}$	4.4	1.99 ± 0.10	≤ 2.0
$\text{C}_6\text{H}_6 + \text{C}_6\text{H}_5\text{I}$ 1.75 $10^{-2}N$	4.0	2.42 ± 0.05	21.4
$\text{C}_6\text{H}_6 + \text{C}_6\text{H}_5\text{I}$ 4.49 $10^{-2}N$	4.3	2.11	15.0
$\text{C}_6\text{H}_6 + \text{C}_6\text{H}_5\text{I}$ 0.112N	4.0	2.10	11.8
$\text{C}_6\text{H}_6 + \text{C}_6\text{H}_5\text{I}$ 0.224N	3.9	2.07	8.0
$\text{C}_6\text{H}_6 + \text{C}_6\text{H}_5\text{I}$ 0.449N	4.1	2.05	7.6
$\text{C}_6\text{H}_6 + \text{C}_6\text{H}_5\text{I}$ 0.898N	4.6	1.86	6.6
$\text{C}_6\text{H}_6 + \text{C}_6\text{H}_5\text{I}$ 1.75N	4.0	1.64 ± 0.10	5.6

in the compounds containing Cl, Br, I, due to positron capture by the halogen. A bound state is formed whose lifetime is of the order of 4×10^{-10} sec. A remarkable reduction of I_2 , with respect to the case of benzene, is also evident for fluorobenzene, but the τ_1 lifetime is identical to the one found for benzene.

While the observed, drastic reductions of I_2 indicated that positron capture by halogens was the leading effect, some positronium quenching could not be excluded, at least in the cases of Br and I compounds. The quenching efficiency of I has been demonstrated in the case of heptane by Hatcher and Millet,¹⁴ and it was therefore considered convenient to investigate the influence of iodobenzene additions to benzene in some detail.

The collected data are given in Table I, and Figs. 2 and 3 show that both positron capture and positronium quenching are effective. The quenching effect is about one order of magnitude smaller than that observed for iodine in heptane, and the $1/\tau_2$ -versus-concentration plot is not linear for small iodobenzene concentrations, while it was found linear for additions of iodine to heptane. Another somewhat confusing feature is that τ_2 is larger for pure iodobenzene than for the iodobenzene-rich benzene-iodobenzene mixtures; this fact is believed to be due to a density effect. The influence on I_2 of C_6H_5I additions to benzene is of the same order as the one found by Ormrod and Hogg¹² for CCl_4 added to benzene, if evaluated on the basis of molar percentages; actually an iodine atom appears to be about ten times more effective than a chlorine atom in capturing a positron.

4. EXPERIMENTAL RESULTS: OTHER HALOGEN COMPOUNDS; DECAY FEATURES OF HALOGEN DERIVATIVES OF BENZENE AT $-100^\circ C$

In Table II are collected the experimental results to be described in the present section.

The liquid compounds ortho- and metadichloro-

TABLE II. Experimental data on halogen derivatives of benzene at low temperature, and on other halogen compounds.

Compound	$\tau_1 \times 10^{10}$ (sec)	$\tau_2 \times 10^9$ (sec)	I_2 (%)	Temperature
Ortho- $C_6H_4Cl_2$	4.1 ± 0.6	2.44 ± 0.10	4.3	room
Meta- $C_6H_4Cl_2$	4.6	2.20	6.4	room
Para- $C_6H_4Cl_2$	5.0	1.70	4.1	room
CCl_4	3.8	2.25 ± 0.20	≈ 1	room
CBr_4	4.6	1.52 ± 0.20	≈ 2	room
$SnCl_2$	4.0	≈ 3	< 1	room
$SnCl_4$	5.3	0.97 ± 0.10	6.8	room
C_6H_6	4.0	1.34 ± 0.10	20.4	$-100^\circ C$
C_6H_5F	4.0	1.26	19.4	$-100^\circ C$
C_6H_5Cl	3.9	1.34	16.3	$-100^\circ C$
C_6H_5Br	3.3	1.52 ± 0.20	2.5	$-100^\circ C$
C_6H_5I	3.0	0.87	≈ 4	$-100^\circ C$

¹⁴ C. R. Hatcher and W. E. Millet, Phys. Rev. **112**, 1924 (1958).

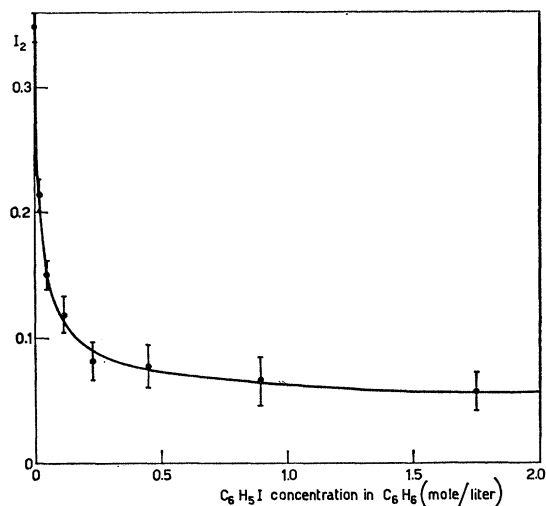


FIG. 2. Dependence of I_2 on C_6H_5I concentration in benzene.

benzene show very similar decay curves; the fact that I_2 is larger for meta-dichlorobenzene is in agreement with the qualitative considerations about the localization of negative charge on the benzene ring which were suggested by the similar case of xylene derivatives.¹⁵ Unfortunately a convincing comparison is not possible with paradichlorobenzene, which is solid. It is also remarkable that I_2 for ortho-, meta-, and paradichlorobenzene is approximately one-half of I_2 for chlorobenzene, which can be readily understood from the fact that the benzene ring contains two chlorine atoms in the indicated compounds.

The leading idea in selecting the other compounds listed in Table II and in investigating benzene and its halogen derivatives in the solid state was that capture of positrons by halogen might become so probable as to prevent positronium formation completely. The purpose of this attempt was to decide whether lifetimes of the order of 10^{-9} sec, typical of the excited states considered by Goldansky *et al.*,⁷ were present. Actually all the examined compounds, which are different in many respects (state of aggregation, nature of the chemical bond, density), showed practically the same short lifetime and weak long lifetimes, whose values were spread within wide limits: No general conclusion could consequently be drawn.

Similarly no evidence of excited levels of positron-halogen compounds could be derived from the data obtained with benzene and its halogen derivatives in the solid state at $-100^\circ C$. Positronium formation does not look particularly unfavored in such materials, at least as far as C_6H_6 , C_6H_5F , and C_6H_5Cl are concerned; moreover the measured values of the short τ_1 lifetime add the confusing feature that they do not seem to depend on the presence of a halogen within the benzene ring. In

¹⁵ J. Green and J. Lee, *Positronium Chemistry* (Academic Press Inc., New York, 1964), p. 75.

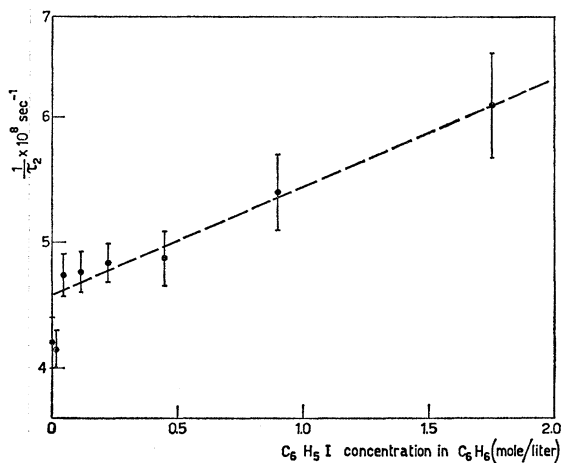


FIG. 3. Dependence of the long lifetime τ_2 on C_6H_5I concentration in benzene.

particular no explanation is available of the fact that the τ_1 lifetime increases from about 2×10^{-10} sec to about 4.0×10^{-10} sec in benzene, when the temperature is decreased to -100°C .

The only case which might be interpretable in terms of excited levels of the positron-halogen compound is the one of solid C_6H_5I which shows two peculiarities: a τ_2 value which is definitely smaller than the ones of the other investigated compounds, and a larger I_2 value.

Anyway it is hard to draw conclusions in the absence

of information concerning the possible temperature dependence of the lifetime of both ground state and excited state of the considered compounds.

5. CONCLUSION

The above reported experimental results seem to indicate that in all the investigated compounds positron-halogen bound states exist, whose lifetimes are about $4-5 \times 10^{-10}$ sec; the only exceptional case is fluoro-benzene. On the other hand no clear evidence was obtained concerning the de-excitation through annihilation of excited states of the positron-halogen compounds; the main difficulty about this point is that in most of the materials investigated positronium formation is not certainly inhibited, not even at low temperature, and there are no arguments to rule out possible effects of positronium quenching.

The measured lifetimes cannot be immediately identified with those reported by Bisi *et al.*,^{2,3} which were dependent on the density of the materials; however it may be pointed out that from the data of Bisi *et al.* the expected lifetimes, for densities like those of the investigated solids and liquids, would be of the order of $4-5 \times 10^{-10}$ sec.

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