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Mössbauer studies of after effects of Auger ionization following internal conversion in organo-^{129m}tellurium compounds

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The after effects of Auger ionization in diphenyl[^{129m}Te]-telluride, dibenzyl[^{129m}Te] telluride, and their dispersions in a solvent at 4.2 K, were compared with the same systems labeled with tellurium in the ground state, viz. ^{129}Te. The Mössbauer emission, in the former case is preceded by Auger event and β decay, while in the latter case, it is preceded only by β decay. Three species were observed in the two compounds, I^-, C_6H_5I or $C_6H_5CH_2I$, and the third one has tentatively been identified as $(C_6H_5)_2I^+$ or $(C_6H_5CH_2)_2I^+$. The formation of I^- represents rupture of both bonds, i.e., complete fragmentation of the molecule. The probability of fragmentation was estimated with the help of matrix isolation experiments, as the electronically excited tellurium-129 ion formed by fragmentation of the molecule, following the Auger ionization, may interact with a neighboring organo-tellurium molecule in neat compounds, and enter combination. In about 85% of the events in case of diphenyl telluride and 55% in case of dibenzyl telluride, molecules escape complete fragmentation despite the fact that about 100 eV excitation energy may be deposited during charge neutralization. A novel mode for rapid disposal of energy is discussed.

INTRODUCTION

The chemical consequences of the Auger event have received wide attention.[1–3] The creation of a vacancy in the inner shell of the atom triggers an Auger event resulting in the ejection of several electrons from the molecule in which it is incorporated. In the gas phase, the redistribution of charges in the molecule leads to multicenter Coulombic explosion with the formation of several fragments.[2,3] In solids, the fate of the molecule can be followed by emission Mössbauer spectroscopy.[4,5] Investigations on cobalt complexes indicate that as a result of the Auger event, the molecules do fragment unless they have a highly conjugated system.[6–11] Nath *et al.*[6–8] have proposed that the higher the degree of conjugation in a molecule, the lower is the probability of its fragmentation. In the Auger event following electron capture decay of cobalt-57 about four electrons are emitted on an average.[12] During subsequent charge neutralization, one would expect that several tens of eV electronic excitation energy would be deposited on the molecule.[7,8] Conjugated molecules somehow survive this super-excitation. We decided to investigate the fate of the molecule, where the metal atom during Auger ionization emits an average of eight electrons and consequently the electronic excitation energy deposited on the molecule during charge neutralization is much higher, and secondly the metal has fewer bonds to conjugated moieties. We have studied the after-effects of the Auger ionization following internal conversion of the isomeric transition of ^{129m}Te in diphenyl, and dibenzyl tellurides. We also observed emission Mössbauer spectra of the same compounds but labeled with the ground state 69 min ^{129}Te. The ^{129}I Mössbauer transition gives information regarding the after-effects, if any, of the mild event, viz β-decay. These spectra constitute reference spectra with which the spectra obtained by compounds labeled with ^{129m}Te are compared. Warren *et al.*[13] had followed this procedure for investigating the after-effects of the Auger ionization in telluric acid and several related tellurium and oxygen compounds.

EXPERIMENTAL

Reactor irradiations

Enriched (>99%) ^{128}Te in the metallic form was irradiated at thermal neutron fluxes of approximately 6×10^{13} n/cm²/s. Short irradiations (approximately 2 h) yielded ^{129}Te with negligible contamination from ^{129m}Te, as reported by Hafemeister *et al.*[14] Irradiations for about 8 weeks were required to obtain ^{129m}Te.

Syntheses of compounds

Diphenyl telluride

The literature procedure[15,16] was adapted. 80 mg of irradiated tellurium and 200 mg of diphenyl mercury were sealed in an ampoule with septum. After flushing with nitrogen, the mixture was heated for 20 min at 220°. The dark yellow liquid was extracted with ether which was allowed to evaporate, and the yellow liquid was syringed into a Mössbauer cup while avoiding diphenyl mercury residue.

Dibenzyl telluride

The procedure was adapted from ones reported in the literature[17,18], it involves the reaction of sodium telluride with benzyl chloride. 3.2 ml of 10% NaOH was added to a mixture of 80 mg of irradiated tellurium and 320 mg

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of sodium dithionite. Hydrogen gas was bubbled through the suspension, maintained at 70°, till almost a colorless solution was obtained (~5 min). 200 $\mu\ell$ of benzyl chloride in 2.8 ml ethanol was added and the mixture was heated for 15–20 min at 70° with continued passage of H_2. The greenish-yellow oily liquid was washed several times with deaerated water and 50% ethanol. Yellow crystals of dibenzyl telluride appeared. Washings and drying of the compound was carried out under nitrogen flow.

Mössbauer measurements

An absorber containing about 15 mg/cm² of $Na^{129}I$ was used. Dehydrated NaI powder was crushed with graphite powder pressed, and encapsulated. Both, the source and the absorber were maintained at 4.2 K. The 27.8 keV Mössbauer transition was detected by a krypton proportional counter using indium filter to attenuate the 29.4 keV x-rays from the absorber.[14]

The data for Mössbauer samples of ^{129}Te was collected for about 3 h, while that for ^{129m}Te was collected over 24 h period. In the latter, the collection of data was started after an interval of about 3 h, so as to permit internal conversion to occur at 4.2 K.

The spectra were analyzed by a least squares fit program based on the procedure reported by Shenoy and Dunlap.[19]

RESULTS AND DISCUSSION

The emission spectra of diphenyl [^{129}Te] telluride, diphenyl [^{129m}Te] telluride, and diphenyl [^{129m}Te] telluride dispersed in ethyl ether are shown in Fig. 1. The computer analyzed Mössbauer parameters for diphenyl and dibenzyl tellurides are given in Tables I and II, respectively. There are three species observed for both the diphenyl and dibenzyl tellurides including the single line, which can be attributed to iodide.

In case of diphenyl telluride, one would expect the daughter iodine to stabilize as iodobenzene or diphenyliodonium, $(C_6H_5)_2I^+$. The reported parameters for [^{127}I] iodobenzene,[20] when converted to ^{129}I with the help of information given in Ref. 21, are as follows: A positive isomer shift, quadrupole coupling −57.7 mm/s, and asymmetry parameter η as 0. The first species (Table I) has parameters matching it, taking into consideration that the sign of the isomer shift and quadrupole splitting for emission spectrum is the reverse of that for the absorption. The spectra of species II (Table I) may be attributed to $(C_6H_5)_2I^+$. The Mössbauer parameters for the diphenyl compound $(C_6H_5)_2\,{}^{129}I^+I^-$ are not reported in the literature. Similarly, species I and II observed in dibenzyl telluride (Table II) may be attributed to $C_6H_5CH_2I$ and $(C_6H_5CH_2)_2I^+$ respectively.

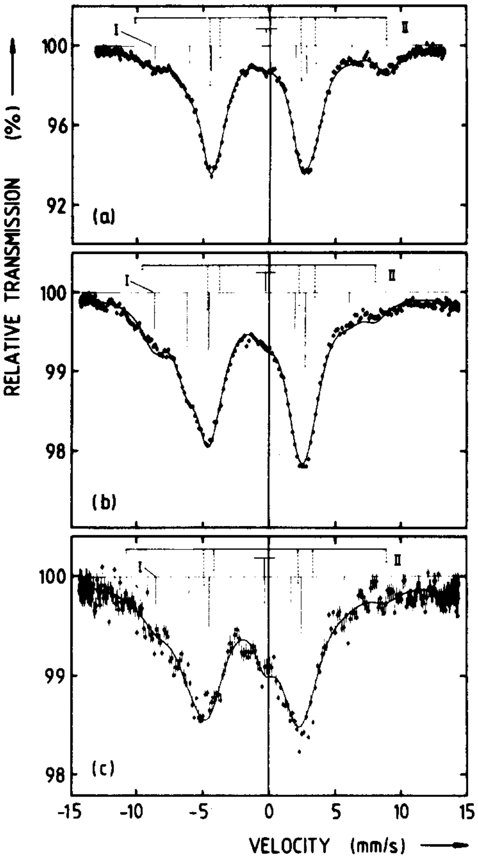

FIG. 1. Emission Mössbauer spectra of diphenyl tellurium; (a) diphenyl [^{129}Te] telluride, (b) diphenyl [^{129m}Te] telluride, and (c) diphenyl [^{129m}Te] telluride dispersed in ethyl ether.

We can now consider the question regarding fragmentation vs nonfragmentation of molecules as a consequence of Auger ionization. The intensities of the three species (Tables I and II) can be compared. $^{129}I^-$ represents rupture of both the carbon–tellurium bonds and hence complete fragmentation of the molecule. The iodide ion is not expected to be as strongly bound in the matrix as the phenyl and benzyl moieties, and therefore the Debye–Waller factor for I^- can easily be less than half of that of the other organic species. On this basis, the apparent probability of fragmentation of the molecules labeled with the metastable tellurium ^{129m}Te is only about 6% as compared to less than 2% for the direct β decay in molecules labeled with ^{129}Te. However, estimation of the probability of fragmentation on the basis of observations on neat compounds only, is not meaningful. Earlier studies[6–8] on cobalt complexes show that a molecule may fragment and the electronically excited daughter $^{57}Fe^{3+}$ or $^{57}Fe^{2+}$ may interact with a neighboring cobalt chelate molecule and undergo exchange. The "reentry" into the coordinated (bound) form can occur in less than 10^{-8} s so that the emission Mössbauer spectra can give the impression as if the molecule did not fragment. To avoid "reentry" we did matrix isolation experiments with dispersions of $(C_6H_5)_2\,{}^{129m}Te$ in ether and of $(C_6H_5CH_2)_2\,{}^{129m}Te$ in ethanol. The diphenyl compound was shown to fragment in about 15% of all Auger events (Table I) and the dibenzyl compound in about 45% of the events (Table II). The phenyl group even when attached to the tellurium atom through CH_2 group exercises considerable stabilizing influence. Mahieu and Llabador[22] have observed the stabilizing influence of benzyl ligands by emission Mössbauer study of $(\text{benzyl})_3\,{}^{119m}SnCl$. Matrix isolation experiment for

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TABLE I. Mössbauer parameters[a] of the three species observed in the emission spectra of diphenyl telluride.

System	Species I		Species II		Species III	
Diphenyl [^{129}Te] telluride	QS	57.0	QS	−55.4	Single line	
	IS	−0.6	IS	−1.2	IS	−0.3
	η	0.1	η	0.5		
	Γ	2.0	Γ	1.7	Γ	1.2
	Int	0.33	Int	0.66	Int	0.007
Diphenyl [^{129m}Te] telluride	QS	58.0	QS	−54.8	Single line	
	IS	−0.6	IS	−1.3	IS	−0.3
	η	0.01	η	0.4		
	Γ	2.2	Γ	2.2	Γ	1.8
	Int	0.63	Int	0.34	Int	0.03
Diphenyl [^{129m}Te] telluride in ethyl ether (1 : 500)	QS	55.0	QS	−56.8	Single line	
	IS	−0.8	IS	−1.5	IS	−0.3
	η	0.1	η	0.5		
	Γ	3.2	Γ	2.7	Γ	2.0
	Int	0.62	Int	0.31	Int	0.07

[a] QS, IS, and Γ represent the quadrupolar splitting, isomer shift, and linewidth respectively, in mm/s. η and Int are the asymmetry parameter and intensity respectively.

this compound has not been reported.

The question arises as to how fragmentation of molecules occurs. The tellurium compounds studied, in contradistinction to cobalt chelates, have only two bonds. Therefore, the possibility of Coulombic fragmentation following Auger ionization cannot be ruled out. If the charge neutralization is very rapid, as is generally the case in solids, then the molecule may escape Coulombic fragmentation. However, as a consequence of charge neutralization following ejection of about eight electrons during the Auger event,[23] we expect deposition of about 100 eV electronic excitation energy. Some of the low energy Auger electrons will be attracted back to the original site, while other electrons (required for neutralization) would come from highly polarized neighboring molecules. The amount of energy deposited on the parent molecule in these two cases would differ as one has to take into account the ionization potential of the polarized molecules in the latter case and so we can only make an approximate estimate of the energy deposited. The energy deposited is certainly very large and should cause rupture of the bonds.[6,7] However, the autoradiolytic model[24,25] assumes that the low energy Auger electrons cause ionization in the ligands, as they traverse inside the parent molecule and they attribute the main Auger after-effects due to this self-ionization. A rough estimate based on the calculations done by Charlton and Booz[26] for ^{125}Te in aqueous matrix, show that about two ionizations may be caused in the parent molecule, diphenyl or dibenzyl telluride, by the Auger electrons. This self-ionization may be regarded as an enhancement of the original Auger event causing loss of 10 electrons instead of 8, from the molecule. However, the important event is the neutralization and thereby the electronic excitation energy deposited on the molecule, an aspect which is not taken into account in the autoradiolysis model.

TABLE II. Mössbauer parameters of the three species observed in the emission spectra of dibenzyl telluride.

System	Species I		Species II		Species III	
Dibenzyl [^{129}Te] telluride	QS	56.6	QS	−50.7	Single line	
	IS	−0.8	IS	−2.0	IS	−0.3
	η	0.05	η	0.42		
	Γ	3.1	Γ	3.1	Γ	2.1
	Int	0.53	Int	0.46	Int	0.01
Dibenzyl [^{129m}Te] telluride	QS	55.0	QS	−52.0		
	IS	−0.7	IS	−1.8	IS	−0.3
	η	0.01	η	0.35		
	Γ	3.2	Γ	2.1	Γ	1.6
	Int	0.73	Int	0.24	Int	0.03
Dibenzyl [^{129m}Te] telluride in ethanol (1 : 500)	QS	55.0	QS	−51.0		
	IS	−0.7	IS	−1.8	IS	−0.3
	η	0.01	η	0.35		
	Γ	3.2	Γ	2.6	Γ	2.1
	Int	0.59	Int	0.19	Int	0.22

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It is surprising how in a fairly large fraction of events, about 85% in diphenyl ^{129m}Te and approximately 55% in dibenzyl ^{129m}Te, the molecules escape fragmentation. The molecule should be able to get rid off its energy very rapidly (~10^{-14} s) if it has to escape fragmentation. The conventional mode of energy transport, viz radiationless transitions in the molecule which permits conversion of electronic excitation energy to vibrational excitation, followed by phonon transport in the lattice, is relatively slow (~10^{-12} s). It is speculated[8] that the energy deposited in a molecule having considerable conjugation goes to excite several π electrons collectively. Then the plasmon can decay in $< 10^{-14}$ s, transferring practically all its energy to a single electron, which is emitted. Decay of a plasmon via electron emission has been observed for aluminum films.[27] This rapid and rather unconventional mode of energy dissipation by the molecule would allow its survival.

It would be interesting to investigate whether π conjugation would offer protection to molecules in the liquid phase. It may have an important bearing for biological systems.[28,29]

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