Inorganica Chimica Acta, *90* (1984) 85–89

A Kinetic and Mechanistic Study of the Photochemical Degradation of a Diarylditelluride in Toluene Solutions Containing Alcohol

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Received February 20, 1984

When toluene solutions containing alcohol and R_2Te_2, where R represents the para-ethoxyphenyl group, are irradiated near the visible absorption maximum of the ditelluride the colour of the solution gradually disappears. The reaction shows a dependence on the presence of oxygen. An induction period is observed when the reaction proceeds under air. Under conditions such that all the incident light is absorbed, the rate of disappearance of the ditelluride is half order in ditelluride, when once the induction period is over. The reaction is also first order in alcohol. The observed rate constant is independent of temperature, within experimental error. Radicals are produced during the irradiation. A reaction scheme is proposed which includes homolytic Te–Te bond cleavage to produce $RTe^{\bullet}$ radicals and a subsequent chain reaction involving alcohol.

Introduction

In this paper we report the results of some studies of the effects of visible radiation on solutions of a diarylditelluride in toluene containing ethanol. These studies were inspired by a chance observation. We found that when solutions of diarylditellurides in laboratory grade chloroform were left on the bench, the solutions changed from brown to colourless. Oxygen, light and the 2% ethanol content proved to be necessary to the process. We studied this process in more detail, using bis-*p*-ethoxyphenylditelluride as the inorganic reagent.

The scientific literature contains several accounts of investigations of the photochemical behaviour of organo-selenium and -tellurium compounds. Thus there are reports [1–3] of various reactions of dialkyl- and diaryl-selenides and tellurides, $R_2'X$ where X = Se or Te. Frequently elemental Se or Te are among the products. The nature of the products is sometimes solvent dependent [1, 3]. In methanol selenides are oxidised by photogenerated singlet oxygen to selenoxides. The irradiation of dibenzyldiselenide has been reported [4–7] in the presence and absence of oxygen. Both C–Se and Se–Se bond cleavage can occur. The cleavage of Se–Se and the formation of EtSe radicals seem [8, 9] to be the most important alternatives in the ultra-violet irradiation of diethyldiselenide.

Spencer and Cava [4] were the first to report results for photoreactions of ditellurides. Dibenzylditelluride and the same diselenide, $PhCH_2XXCH_2Ph$, behave similarly upon UV irradiation. The reactions have been studied in the presence [4] and absence [4, 10] of oxygen. In the presence of oxygen the ditelluride yields PhCHO, $PhCH_2OH$, $PhCH_3$, $PhCH_2CH_2Ph$ and elemental Te. In the absence of oxygen, dibenzyltelluride and tellurium are produced [11] quantitatively. All these observations are explained by the initial cleavage of Te–C bonds. Pulse radiolysis experiments [12] on $R_2'X$ and R′XXR′ have been interpreted as showing the production of R′Se, R′SeSe and R′Te radicals.

Therefore under the conditions of our experiments we may reasonably expect the formation of radicals of some sort to occur.

Results

Except where specifically stated, all our findings refer to the reagent bis-*p*-ethoxylphenylditelluride. We have followed the effect of light, dioxygen and ethanol on this compound by using toluene as a solvent and monitoring the reagent concentration at 395 nm.

In Fig. 1 we reproduce experimental plots of ditelluride concentration against time for irradiated solutions under air, almost pure oxygen and nitrogen. Unfortunately the design of our apparatus for kinetic studies is such that some air will have been admitted to the apparatus even when we have attempted to obtain atmospheres of a pure gas. The plots show that an induction period occurs under air, is longer under almost pure nitrogen and is almost undetectable

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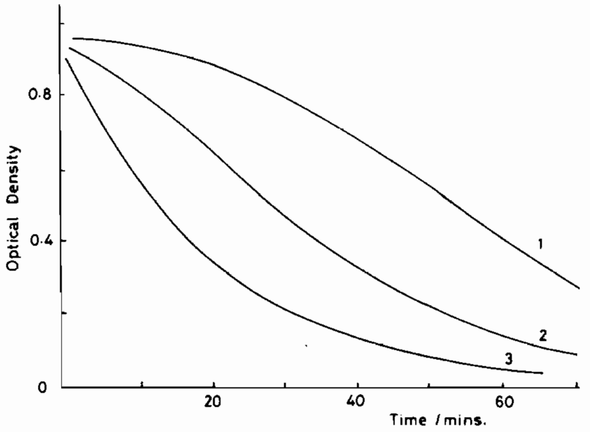

Fig. 1. The observed variation of optical density with time for reaction solutions irradiated under atmospheres of: 1) predominantly nitrogen; 2) air; 3) predominantly oxygen.

under oxygen. The rate of the subsequent reaction also depends on the oxygen concentration, but the dependence is neither linear nor very pronounced. We were unable simultaneously to rigorously exclude oxygen from a solution, and to continuously monitor its optical density. Therefore, the majority of our observations were carried out under air.

In order to study the effect of total oxygen exclusion, we undertook some experiments using a sealed system from which samples could be abstracted without the admission of any unwanted air. We were thus able to demonstrate the need for oxygen to be present. We chose conditions of illumination, such that the decolorisation of a solution of ditelluride in 20% ethanol/toluene, under air, was approximately 90% complete within 90 minutes. Experiments differing only in the rigorous exclusion of oxygen, and its replacement by nitrogen, showed no change in optical density over a period of 60 hours.

When once the induction period is over, the reaction profile in the presence of oxygen is described by eqn. 1 to at least 75% completion

$$[R_2Te_2]^{1/2} = \text{constant} - k_{obs}t \qquad (1)$$

The value of k_{obs} thus determined is reproducible to within 5% for the same conditions and apparatus configuration. In Table I we quote observed rate constants for the curves shown in the figure.

The data collected by us as the temperature, ethanol concentration and type of alcohol used were varied are quoted in Tables II, III and IV respectively.

Our chosen light source was a 60 watt domestic lamp, placed at a fixed position relative to the flask containing the bulk of the reaction solution. Such a lamp emits a wide spectrum. The interposition of various filters enabled us to show that the exciting wavelength is close to 400 nm. That is, at or near the visible absorption maximum of the ditelluride. We

TABLE I. Observed Rate Constants at 25 °C under Different Gaseous Atmospheres at Atmospheric Pressure, Other Conditions Being Standard.

Atmosphere	$10^3k/mol^{1/2}\ dm^{-3/2}\ min^{-1}$
Air	0.36
Nitrogen[a]	0.20
Oxygen[a]	0.47

[a] Some air will have leaked into these experiments.

TABLE II. The Variation of the Observed Rate Constant with Temperature.

T/°C	$10^3k/mol^{1/2}\ dm^{-3/2}\ min^{-1}$
20.0	0.38
25.0	0.35
30.0	0.41
35.0	0.40
40.0	0.39
45.0	0.40
50.0	0.40
55.0	0.34

TABLE III. The Variation of the Observed Rate Constant with the Ethanol/Toluene Ratio of the Solvent.

%EtOH by volume	[EtOH]/ $mol\ dm^{-3}$	$10^3k/mol^{1/2}\ dm^{-3/2}\ min^{-1}$
7.5	1.28	0.10
10.0	1.71	0.13
12.5	2.14	0.17
15.0	2.57	0.23
17.5	3.00	0.27
20.0	3.43	0.32
22.5	3.85	0.33
25.0	4.28	0.35
27.5	4.71	0.39
30.0	5.14	0.45
32.5	5.57	0.47
35.0	5.99	0.52

TABLE IV. The Effect of Different Alcohols on the Observed Rate Constant. Other conditions standard. In each case the alcohol is 25% by volume.

Alcohol	[ROH]/ $mol\ dm^{-3}$	$10^3k/mol^{1/2}\ dm^{-3/2}\ min^{-1}$
methanol	6.34	0.39
ethanol	4.28	0.36
1-propanol	3.35	0.36

have used solutions of $k_3[Fe(ox)_3]\cdot3H_2O$ for actinometry. By following the prescribed procedures [13] we have been able to assess the efficiency of our process. Given the variation of the rate of loss of reagent with its concentration, it is only appropriate to write of 'instantaneous' quantum yields. We find that, when the rate of decolourisation is at its greatest, the quantum yield is 0.7. At other stages it is, of course, less.

When the illumination of a reaction solution is stopped, the optical density ceases to change. The reading remains steady for several hours, at least. When a solution of bis-*p*-ethoxy-ditelluride at a much higher than usual concentration in toluene, 5×10^{-3} *M*, is irradiated in the presence of a small amount of ethanol and the decolourised solution then concentrated under vacuum, an oily white product can be obtained, which analyses to $(EtOC_6H_4Te)_2O$. Similarly, the bis-phenylditelluride gives $(PhTe)_2O$. In the latter case there is no indication of aliphatic C–H in the infra-red spectrum, but both products show broad bands characteristic of Te=O between 750 and 550 cm^{-1}.

Thin layer chromatography of reaction solutions on silica gel always shows only one detectable coloured spot. When decolourisation is complete some eluents, toluene or toluene/chloroform mixtures, show the presence of two different colourless solutes. When a typical reaction solution is irradiated beyond the end of the induction period an esr signal is detectable. The species producing this signal is fairly long lived as it can be detected after irradiation of a sample inside the esr cavity, or after irradiation in our normal apparatus and subsequent transfer to an esr sample tube. This signal is seen only when a solution of the ditelluride is irradiated in the presence of oxygen. Ethanol is not necessary for its appearance. The signal is very broad, with a g value of 2.017 gauss and is unaffected by the presence of the spin-trap N-tert-butyl-alpha-phenyl-nitron. A solution of diarylditelluride in tetrahydrofuran, when treated with lithium under nitrogen in the dark [14], with the spin-trap present, gives a similar broad esr signal with g = 2.014 gauss. The reaction between equimolar amounts of *p*-phenetylbromide and butyllithium under nitrogen in anhydrous conditions results in a totally different esr signal when the spin-trap is present.

The most straightforward interpretation of these observations is that the radical RTe is formed under our experimental conditions and that little or no Te–C cleavage occurs.

Discussion

We have worked with concentrations of ditelluride which give optical densities of approximately unity at 395 nm for a 1 cm flowthrough cell at the start of a reaction. The configuration of our apparatus is such that essentially all light incident on the reaction flask passes through at least 5 cm of reaction solution. Even when the disappearance of the ditelluride is 80% complete, at least 90% of incident light at 395 nm will be absorbed by the reaction solution. Therefore we can assume that the initial excitation

$$R_2Te_2 \xrightarrow{h\nu} R_2Te_2{}^* \ldots\ldots k_0$$

is zeroth order in the ditelluride throughout the observed course of the reaction.

Our esr findings, together with the half order rate equation for the loss of optical density show that a homolytic Te–Te bond cleavage, yielding $RTe^\bullet$ radicals, must occur. Since the overall reaction is not independent of the ditelluride concentration, two ditelluride molecules must be involved in this radical production. Molecular oxygen is also involved at an early stage in the reaction sequence.

The first five steps of our proposed scheme would produce the required mathematical form of the rate equation, and are in agreement with our findings concerning dioxygen and radicals. Unfortunately they do not represent a unique solution. Alternatives introducing two ditelluride molecules, dioxygen and a quantum of light in a different order can be devised. We prefer this sequence, but cannot prove it.

In our experiments we are dealing with a reaction sequence involving radicals. The instantaneous quantum yield can be as high as 0.7; while the overall activation energy is zero, within experimental error (see Table II). Therefore we feel that the overall process must involve a radical chain reaction. The overall reaction is also first order in ethanol (see Table III). Substitution of phenol or t-butanol for ethanol prevents the occurrence of any reaction, while methanol and n-propanol allow the decolourisation of the solution to occur. The later steps of the scheme satisfy these additional requirements, as long as the steady state hypothesis can be applied to the concentrations of $R_2Te_2{}^*$, $R_2Te_2O_2$, $RTe^\bullet$ and $R'CHOH$. If the terms due to k_8 and k_9 are unimportant, then this scheme gives, as the overall rate equation,

$$\frac{-d[R_2Te_2]}{dt} = 2k_5\sqrt{\frac{k_0k_2k_4[O_2]}{k_3k_7(k_1 + k_2[O_2])}}\cdot[R'CH_2OH][R_2Te_2]^{1/2}$$

The products shown in that scheme are not the final products isolated by us. We finally isolate $(RTe)_2O$. Therefore the RTeH and RTe(CH(Me)OH), can only be metastable. In view of the known chemical properties of organotellurium compounds, that is very reasonable.

$$R_2Te_2 + h\nu \xrightarrow{k_0} R_2Te_2^*, \text{ zeroth order in } [R_2Te_2]$$

$$R_2Te_2^* \xrightarrow{k_1} R_2Te_2$$

$$R_2Te_2^* + O_2 \xrightarrow{k_2} R_2Te_2O_2$$

$$R_2Te_2O_2 \xrightarrow{k_3} R_2Te_2 + O_2$$

$$R_2Te_2O_2 + R_2Te_2 \xrightarrow{k_4} 2RTe^\bullet + R_2Te_2 + O_2$$

$$RTe^\bullet + CH_3CH_2OH \xrightarrow{k_5} RTeH + CH_3CHOH$$

$$R_2Te_2 + CH_3CHOH \xrightarrow{k_6} RTeCHCH_3OH + RTe^\bullet$$

$$2RTe^\bullet \xrightarrow{k_7} R_2Te_2$$

$$2CH_3CHOH \xrightarrow{k_8} CH_3CHOHCHOHCH_3$$

$$RTe^\bullet + CH_3CHOH \xrightarrow{k_9} RTeCHOHCH_3$$

Scheme

Experimental

All organic solvents were dried and redistilled by recommended methods [15] before use. When deoxygenated solvents were required, they were degassed by the freeze/thaw method. All tellurium containing reagents were prepared from tellurium tetrachloride (B.D.H.) by literature methods [16, 17]. Analytical and melting point data are collected together in Table V.

The reaction product, bis-(*p*-ethoxyphenyltellurenyl)oxide, was prepared by irradiating a solution of the parent ditelluride in dry toluene (5×10^{-3} *M*) under air using visible radiation from a tungsten lamp. When the solution had become colourless, the bulk of the solvent was removed under reduced pressure and the white product was dried under vacuum.

Kinetic studies were carried out using a double-walled glass round bottomed flask (approximately 100 cm^3 capacity), with water from a thermostat bath circulating through the outer compartment. Reaction solution was pumped peristaltically from this flask through a 1 cm flow-through spectrophotometer cell and then back into the main flask. The flask was mounted on a rigid support. At a distance of 6 cm below the bottom of the flask a 60W tungsten lamp was fixed and the whole assembly then surrounded by a light tight box. The flexible tubing serving the peristaltic pump was of the minimum practical length, and was frequently replaced. The entire apparatus was thoroughly flushed out and cleaned after every run. For the majority of experiments the apparatus was charged in the open laboratory. When an atmosphere of essentially pure oxygen or nitrogen was required, the main flask was filled under the appropriate atmosphere: the tubing of the flow circuit was separately filled under that gas and the two sections finally united. Given our experimental design, there is no way of avoiding the admission of small amounts of air when the two parts are united.

When the total absence of oxygen was required a single walled flask was used, without an attached peristaltic circulation system. The solution was thoroughly flushed with white spot nitrogen for at least one hour, and finally studied under a slight positive pressure. Samples for spectrophotometric examination were occasionally withdrawn through a double-topped side-arm and were not returned to the main bulk afterwards.

Acknowledgement

Two of us (Rahim T. Mehdi and Tahir A. Tahir) wish to thank the Iraqi Government for the provision of studentships.

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TABLE V. Elemental Analytical Data.

Compound[a]	% Found			% Calcd			m.p/°C		
	C	H	Te	C	H	Te	found	lit.	Ref.
$RTeCl_3$	27.0	2.5		27.1	2.6		184–6	182–3	16
R_2Te_2	38.5	3.6	51.3	38.6	3.6	51.3	102–4	107–8	16
Ph_2Te_2	35.3	2.5	62.3	35.3	2.5	62.3	65–6	66–7	17
R_2Te_2O	37.7	3.6	50.0	37.5	3.5	49.5	150		

[a] R represents *p*-ethoxyphenyl.

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