PHOTOCONDUCTIVITY OF DEGASSED ETHERS AS A FUNCTION OF THEIR PURITY

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Summary

The pulse d.c. photoconductivity (PC) of the vacuum-degassed ethers tetrahydrofuran (THF), ethyl ether (Et_2O) and 1,4-dioxane was investigated. It was found that after a light pulse of duration 1 ms in degassed THF or Et_2O the photocurrent rises. A monophotonic ionic photodissociation is responsible for the charge generation since the photosignals were proportional to the amount of absorbed light. The photocurrent signals decreased exponentially with first-order rate constants which decreased linearly with the decreasing voltage applied between the platinum electrodes. This might indicate that the fairly stable photoproduced ions disappear mainly in the electrode discharge reactions. The bulk recombination, which is probably preceded by a monomolecular or pseudomonomolecular rearrangement (since this is a process also well described by an exponential equation) did not exceed about 10% of the total ion consumption under the conditions used. After examining different methods of purification of the ethers studied it was found that the phenomenon was caused by electron acceptor impurities, which were mainly the products of the oxidation of ethers. In the case of 1,4-dioxane the PC signals were hardly detectable, since the lower polarity of this solvent did not favour ionic dissociation of the ion pairs which are probably also produced. An improved method of purification of these ethers is proposed.

1. Introduction

Ethereal solutions of some nitro and halogeno compounds show a positive photoconductivity (PC) phenomenon [1 - 6] on exposure to UV−visible light that can be absorbed by the solutions. Many other investigations, including photocurrent measurements, have been carried out on n−π systems in glasses and in solutions using ethers as n donors [7 - 10]. It is often assumed that solvents (ethers) do not contribute to PC effects, at least to a significant degree. The situation may change when a pulse technique and polychromatic light sources are used. The possibility of biphotonic processes

can become considerable, yet the main difference is caused by the higher light densities. Therefore, an enhancement of the effects can be expected depending on this parameter. In such a case the neglect of the PC of ethers might be unjustified.

Simple ethers are widely used in many fields of scientific activity. It is well known that they are quite susceptible to reaction with molecular oxygen via postulated charge transfer or contact charge transfer complexes [11]. Irradiation makes these processes faster and more significant and leads to many photo-oxygenation products [12 - 17]. However, physicochemical investigations very often require a high degree of purity of solvents. Thus, the problems associated with the methods of purification of solvents and their storage as well as the means of establishing their degree of purity are still current [18 - 20].

It is apparent that the degree of purity of degassed ethers plays a dominant role in their PC and these problems drew our attention.

2. Experimental details

2.1. Apparatus

The PC measurements were carried out using an assembly which is shown schematically in Fig. 1. It consists of an electric circuit A and a flash lamp system B. The electric measurement system is formed by connecting in series a high voltage d.c. power supply (ZWN ± 4 kV), the PC cell and an exchangeable standard resistor. A signal taken from the resistor was recorded on an oscilloscope (STD 501 XY) and/or on $X-Y$ recorders (TZ 4200, KP 6801A XY).

The quartz cell shown in Fig. 2 enables high vacuum degassing of liquid samples to be carried out. A sample was put in the bulb marked A and degassed in several freeze—pump—thaw cycles using another vacuum line. Then the evacuated cell was closed (or sealed off) and the sample was poured into the PC measuring compartment B having two platinum electrodes (Pt). The cell constant for the electric conductivity was 2.02 cm^{-1}. During the PC stabilization period the solution of NaCl in water was usually flowed through a cooling jacket. The procedure not only enabled a desired temperature to be maintained but also considerably reduced, by earthing the coolant solution, the electrical noise, which was especially important when weak signals were recorded.

The flash lamp system consists of a d.c. power supply (up to 12 kV), condenser banks (50 μF), a quartz tube 6 cm long such as a flash lamp, a manometer, a system of cocks and a rotary vacuum pump. The system could work under steady or under flow conditions.

The lamp and the properly prepared PC cell were placed in the foci of a mirrored elliptic reflecting screen (part C in Fig. 1) in such a way that the electrode surfaces were not illuminated. By controlling the pressure of gas in the lamp and changing the voltage on the condenser bank the pulse light
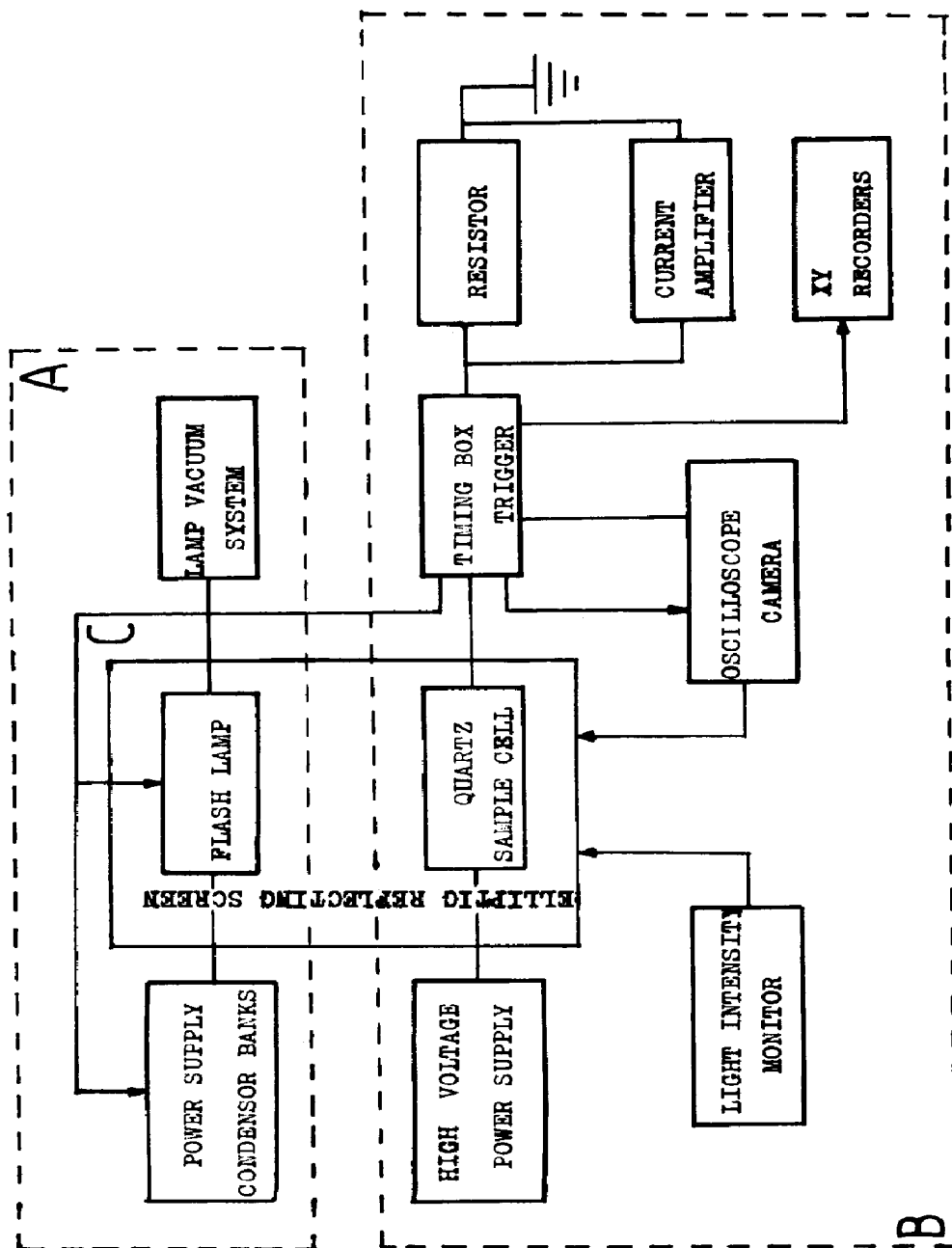
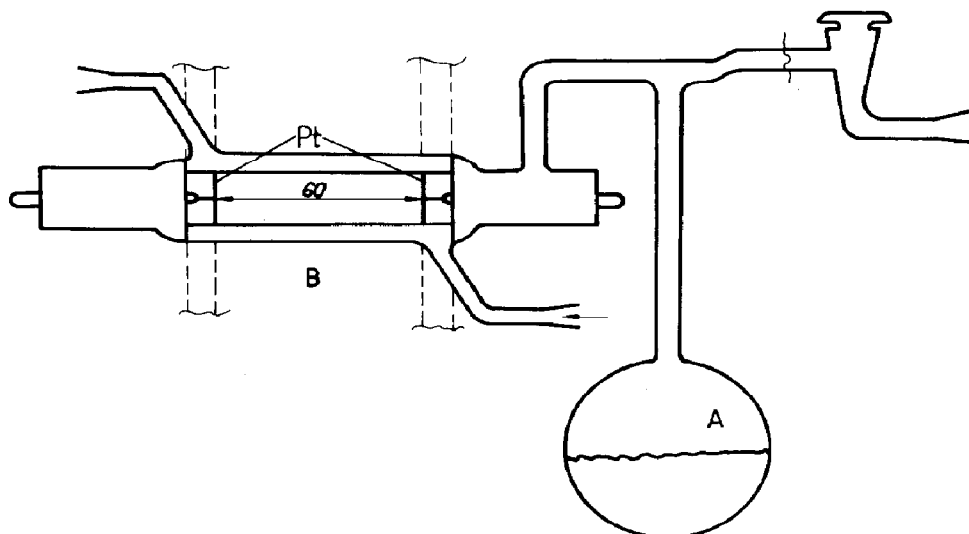Fig. 1. Schematic diagram of the PC apparatus.

Fig. 2. Quartz PC cell: Pt, platinum electrodes; A, the bulb for vacuum degassing; B, PC measurement chamber surrounded by a cooling jacket.

intensity could be regulated. The dependence of the light intensity on the electric energy stored in the condenser bank is shown in Fig. 3. The amount of light was monitored using an alcoholic solution of malachite green as an actinometric medium. To carry out the actinometric measurements the cell was filled with malachite green solution, put inside a housing C and then exposed. Since the absorption region of the actinometer covers that of the ethers (see Fig. 4), the recorded relationship allowed us to measure the
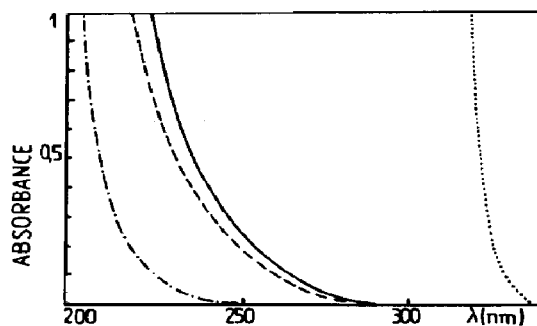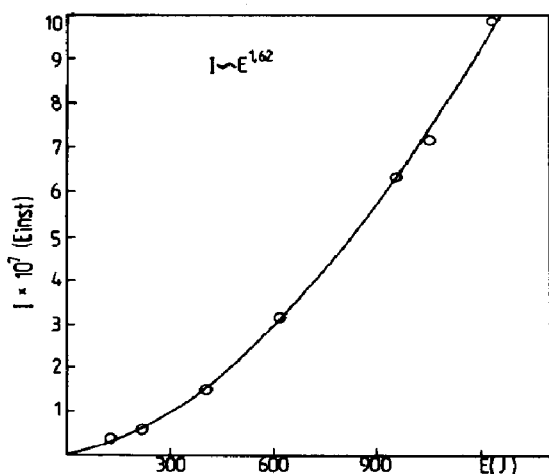

Fig. 3. The flash pulse intensity I measured actinometrically as a function of the electric energy E stored in the capacitor bank.

Fig. 4. A plot of absorbance vs. wavelength for various freshly distilled ethers and for the actinometric solution: — — —, 1,4-dioxane; ———, Et_2O; — · — ·, THF; ············, actinometric solution.

relative PC yields as well as to estimate the extent to which the process of charge generation is photonic.

The timing unit (Fig. 1) enabled us to synchronize a flash with a run on the oscilloscope. Just before triggering, a resistor of the same value as the input resistance of the oscilloscope was switched off, a photocurrent trace on the oscilloscope was recorded, then the oscilloscope was switched off and the recorders were started again. This procedure allowed us to eliminate the influence of polarization currents on the photosignals, which were measured against a background of the stabilized value of the dark current. The electric circuit response time was at least about 200 times shorter than a flash duration ($\tau = 1$ ms). However, the photocurrent growth time was of the order of tens of milliseconds, so it was affected by the effects on the electrodes of the cell rather than by the parameters of the apparatus.

2.2. Purification of ethers

The ethers THF, Et_2O and 1,4-dioxane, all of the purest available grade, were further purified using mainly one of the three following procedures.

(a) After the preliminary removal of water (by treating with potassium hydroxide) the solvents were refluxed for about 12 h over lithium aluminium hydride and then distilled. A middle fraction was kept and used immediately for further experiments.

(b) After preliminary drying, the ethers (THF and 1,4-dioxane) were refluxed for 12 h over potassium or, in the case of Et_2O, over Na–K alloy. They were then distilled and used as in method (a).

(c) The new step of photoiodination was introduced as follows. A 2 dm^3 bulb made of Pyrex glass was filled with purified ether and iodine (about 2 g) and saturated hydrochloric acid (1 cm^3) were added. The solution was refluxed for about 6 h and at the same time was exposed to a full light flux from a medium pressure mercury lamp (Q-400 Hanovia). The purpose of this operation was to insert a heavy atom into carbonyl or olefin impurities in order to remove them subsequently in a distillation process. Potential traces of iodocompounds still present after distillation should be decomposed while refluxing over a reducing agent during further operations. The THF and Et_2O thus prepared were distilled, a middle fraction was kept, dried and then treated as in method (b). In the case of 1,4-dioxane, its complex with iodine has a tendency to creep up a distillation column, so it was necessary to remove the excess of unreacted iodine. To do this the solution was cooled, some iron powder and hydrochloric acid were added and the mixture was stirred for some time. After the operation, iodine should not be detectable with a starch probe. Afterwards the decanted solution was distilled, and a collected fraction, after preliminary drying, was then used as in method (b). Some batches of 1,4-dioxane containing aromatic impurities were crystallized in a preliminary step (melting point, 285 K).

In the distillation procedures a distillation column (length 1 m) filled with glass beads was used as well as other necessary standard Quickfit

equipment. All operations requiring heating were carried out in deoxygenated argon, and all pipes transporting argon were made of Teflon.

The degree of purity of the ethers was checked by the following methods: (i) gas chromatography (GC) (Pye–Unicam Model 104, packed columns, mainly PEG 20M, Chromosorb 102 and 103 at different temperatures); (ii) UV absorption (Specord UV–visible, Carl Zeiss, Jena); (iii) PC and conductivity measurements of degassed and non-degassed ethers.

It turned out that among the methods of purification method (c) gave the best results, being particularly advantageous for Et_2O.

3. Results

The photosignals were recorded after polarization currents had settled to a constant dark value. This usually took about 0.5 h and during that time the sign of the d.c. polarization voltage applied to the electrodes was changed periodically. The flash excitation of THF and Et_2O resulted in photocurrent signals which usually consisted of two components: (i) a faster one, whose contribution to the overall signal was more pronounced in THF yet its maximum value did not exceed 10% of the total increase, and (ii) a slower one, whose duration depended on the conditions used (see later). Typical traces are shown in Fig. 5. The best kinetic description of the entire relaxation was achieved when the first-order rate equation was used. The linear correlation coefficients for the relationship $\ln \Delta\kappa = -kt + \ln \Delta\kappa^0$, where $\Delta\kappa$ (Ω^{-1} cm^{-1}) denotes an increase in the electrical conductivity, were always higher than 0.988 and the intercepts estimated were about 10% lower than those measured at the peak photocurrent. Applying a second-order rate equation always gave a worse fit. The kinetics of relaxation of the faster component did not correlate with any physicochemical parameters, probably because of the chemical instability being dependent on the history of the sample.

Electrode processes did not contribute to the charge generation responsible for the photocurrent. This was as expected, since the electrodes were not illuminated and an enhancement of the dissociation of a precursor
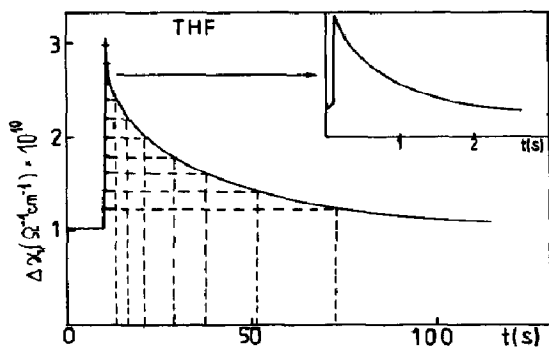

Fig. 5. Typical PC decay in degassed THF purified by method (a).

complex in an electric field requires a much higher value of the electric field intensity [21, 22]. The lack of dependence of the PC yield on the d.c. voltage applied between the electrodes is shown in Fig. 6. This conclusion is also supported by the sampling method, which is described later.
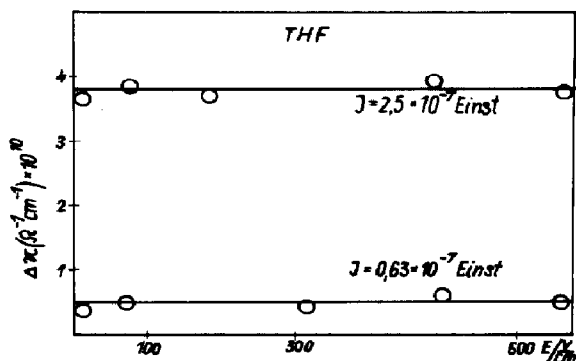

Fig. 6. The PC of degassed THF as a function of the electric field intensity.

The dependence of the peak intensity of the signals on the flash energy measured actinometrically always gave a straight line (Fig. 7). The different slopes are due to different relative PC yields caused by different purity levels of the ethers. The PC yields are relative because uncertainties in several aspects of the measurements such as the cylindrical cell calibration, the different refractive indices for the ethers and for the actinometric solution and the different absorption regions (only the absorbance of the ethers is covered by that of the actinometer) did not allow us to make strictly quantitative
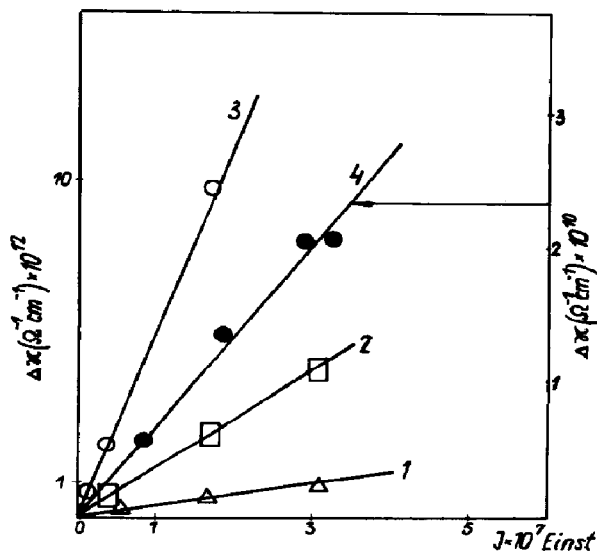

Fig. 7. The PC of degassed samples of Et_2O vs. light intensity: line 1, freshly distilled Et_2O purified by method (c); line 2, the same ether after storage for a week; line 3, the same Et_2O after 1/2 h exposure to UV radiation; line 4, PC of Et_2O purified by method (a) (left-hand side scale).

comparisons. Nevertheless, they appeared to be very useful in establishing qualitative associations, and they also helped us to elucidate to what extent the charge generation process is photonic.

To make sure that potential iodocompounds did not affect PC signals for the sample of Et_2O purified by method (c), iodoethane was added in an amount that was not detectable by GC or by a spectral method in the same way as for the purest ether. This caused a considerably higher dark current, and at the same time the PC signals were hardly detectable and had quite a different shape. Such behaviour has never been observed for degassed ethers, which again seems to confirm that the photoiodination step is unlikely to introduce additional impurities.

The first-order rate constants for the overall decay of the PC were dependent on the d.c. voltage V applied between the electrodes, giving a linear relationship (Figs. 8 and 9). The value of the rate constant k for $V = 0$ describes the rate of the bulk consumption of charge carriers and is denoted here as k_2. It was interesting to elucidate the character of the bulk recombination process. The first assumption was that this disappearance is a simple recombination governed by the two-body recombination law. For such a case the overall relaxation process should be a better fit, especially for a low d.c. voltage, when bulk recombination and electrode discharge were consuming similar amounts of ions according to the following equation:

$$-\frac{d \Delta\kappa}{dt} = k_1 \Delta\kappa + k_2(\Delta\kappa)^2 \tag{1}$$

where $\Delta\kappa$ is the change in photoconductivity and k_1 and k_2 are the electrode discharge and recombination rate constants respectively. Solving this equation and rearranging it to a linear form

$$\frac{k_1 \exp(-k_1 t)}{\Delta\kappa} = \frac{k_1}{\Delta\kappa^0} + k_2\{1 - \exp(-k_1 t)\} \tag{2}$$

and substituting for k_1 from the voltage dependence should give the k_2 value. However, we have found that such a description does not agree with the experimental data. To solve the problem, a sampling method was used and it was performed as follows. After a sample had stabilized, the high voltage (HV) electrode was mechanically switched off, the sample was immediately exposed, and the HV electrode was then switched on again. The PC signals had the same intensity as those measured against a background of a permanently flowing dark current. This also confirmed that electrode processes did not contribute to PC yields.

The same procedure could be used as a way of establishing the kinetic order and the rate constant value for the disappearance of bulk charge carriers, which was independent of electrode discharge reactions. In this case the HV electrode was switched on after a different time. For a series of flashes having the same energy, peak signal intensities were recorded and correlated with time. It was also necessary to repeat the same procedure when there were no flashes in order to elucidate and to compensate for the
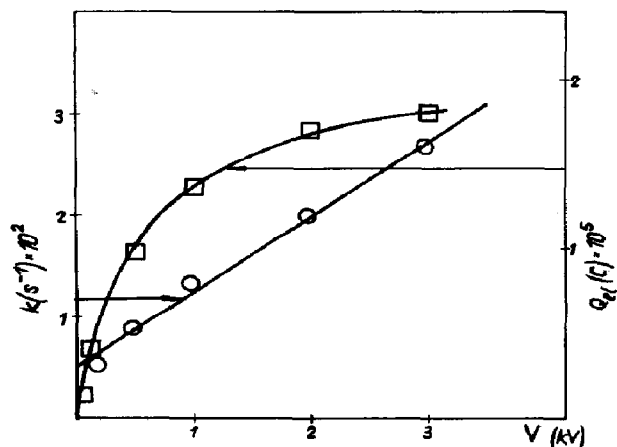
Fig. 8. Rate constant of PC relaxation in THF (left-hand side scale) and electric charge that flowed through the circuit (right-hand side scale) vs. d.c. voltage applied between the electrodes ($\Delta\kappa^0 = 1.2 \times 10^{-10}\ \Omega^{-1}\ cm^{-1}$; $T = 25\ °C$). Parameters of $k = f(V)$: $r = 0.998$; $k_2 = 4.68 \times 10^{-3}\ s^{-1}$; $\mu = 2.8 \times 10^{-4}\ cm^2\ V^{-1}\ s^{-1}$. Parameters according to eqn. (3): $r = 0.999$; $k_2 = 4.1 \times 10^{-3}\ s^{-1}$; $\mu = 3.2 \times 10^{-4}\ cm^2\ V^{-1}\ s^{-1}$.
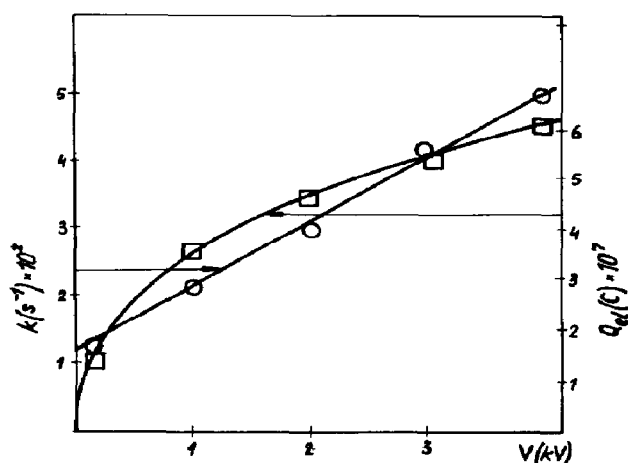

Fig. 9. Rate constant of PC relaxation in Et_2O (left-hand side scale) and electric charge that flowed through the circuit (right-hand side scale) vs. d.c. voltage applied between the electrodes ($\Delta\kappa^0 = 1.6 \times 10^{-11}\ \Omega^{-1}\ cm^{-1}$; $T = 20\ °C$). Parameters of $k = f(V)$: $r = 0.998$; $k_2 = 1.06 \times 10^{-2}\ s^{-1}$; $\mu = 3.55 \times 10^{-4}\ cm^2\ V^{-1}\ s^{-1}$. Parameters according to eqn. (3): $r = 0.998$; $k_2 = 4.22 \times 10^{-3}\ s^{-1}$; $\mu = 1.37 \times 10^{-4}\ cm^2\ V^{-1}\ s^{-1}$.

growth of the dark current owing to depolarization effects caused mainly by diffusion of electric double layers (see Section 4).

It was found that the bulk charge carrier consumption was well described by the first-order rate equation. The rate constant values estimated from the simple $k = f(V)$ relationship are prone to be erroneous since a small deviation in the slope of a $k = f(V)$ line results in a significant change in the k_2 value.

A more precise way of estimating the k_2 value is accomplished by measuring the electric charge that flows through the circuit. (Figs. 8 and 9). If

there had not been any bulk disappearance, the relationship $Q = f(V)$, where Q is the electric charge, would have been a straight line parallel to the x axis. The actual plots are shown in Figs. 8 and 9, and hence such consumption does take place.

Knowing that this disappearance is also exponential and carrying out the measurements carefully, it was possible to elucidate the k_2 value from the $Q = f(V)$ dependence. The Q value measured as an area under the $i = f(t)$ curve for exponential relaxation is given by $Q = \int_0^\infty i \, dt$ which is i^0/k because $k = k_1 + k_2$ and $k_1 = aV$ (Figs. 8 and 9) and $i^0 = V/R^0$, where V is the d.c. voltage from the power supply and R^0 is the resistance of the sample at the peak photocurrent (i, current; a, constant). For n runs

$$\frac{1}{Q} = \frac{k_2}{n} \sum_1^n R_n{}^0 \left(\frac{1}{V}\right) + \frac{a}{n} \sum_1^n R_n{}^0 \tag{3}$$

The reciprocal of the electric charge plotted against the d.c. voltage gives a straight line, whose slope is proportional to the k_2 value. The k_2 values estimated by these means range between 0.4×10^{-2} and 1×10^{-2} s^{-1}.

It was also found that the k_1 values measured at constant voltage depended on the total amount of charge carriers generated in a sample (Fig. 10). This means that the more ions are produced the slower their disappearance on the electrodes. The problem of the disappearance of fairly stable ions in moderately polar liquid media has been investigated in a more chemically defined system consisting of symmetric trinitrobenzene in THF [23, 24].
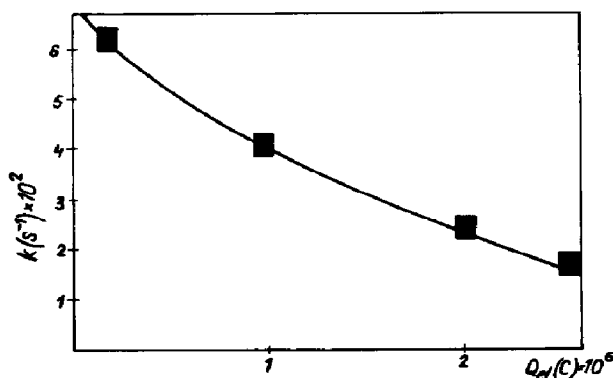

Fig. 10. Rate constant of PC relaxation in degassed THF as a function of the electric charge initially photoproduced in the sample. Voltage between the electrodes, 4 kV.

4. Discussion

For all samples of ethers showing the PC phenomenon the relation $\Delta\kappa^0 = f(I)$ was always linear, which might indicate that the charge generation process is monophotonic. However, the energy of the radiation used (above

200 nm) is not enough to cause efficient monophotonic photoionization of the ethers studied, which have ionization potentials in the gas phase higher than 9 eV [25]. Even the typical lowering of the ionization threshold in the liquid state [26 - 28] would not be enough. Thus, charge carriers must have been formed in the ionic photodissociation process of any precursor complexes formed between electron acceptor impurities and ethers as n donors (see later). Such processes usually require much lower energy [29, 30] and give ions without passing though a stage involving quasi-free electrons. This assumption is partly confirmed by mobility measurements which gave the mobility values typical for ions. As has been pointed out above, the magnitude of the PC effect depended on the purification procedure, yet for samples purified in the same way the absolute PC yields were similar. Thus, it was not the nature of these solvents that was responsible for the above phenomenon but rather the effect was caused by some impurities present in the ethers. This suggestion was also supported by other evidence, which to some extent shed light on the chemical character of these impurities (see Fig. 7). Namely, when the well-purified ether (method (c)) (for Et_2O the effect can be clearly seen, since its dark conductivity is about three orders of magnitude lower than that for THF) was stored for a week in a closed bottle kept inside a dark desiccator with P_2O_5, but oxygenated during the pouring operation, then after degassing its PC increased as indicated by line 2 in Fig. 7. When the same sample of the purest ether (line 1) was refluxed and exposed to UV light in a quartz bulb for 0.5 h in the presence of oxygen, then after degassing its relative PC yield increased about 20 times (Fig. 7, line 3). This may prove that oxygenation and photo-oxygenation products are the main impurities responsible for the PC phenomenon in degassed ethers.

An attempt to establish the nature of these impurities was undertaken. Acetone and propyl formate, as representatives of typical carbonyl compounds, were added to the well-purified Et_2O. After degassing, the solution showed an enhancement of PC but its magnitude was inadequate at the concentrations of additives easily detectable by chromatography. Chromatographically purer Et_2O but purified by method (a) exhibited a larger PC. It seems that the reported PC phenomenon in degassed ethers (THF, Et_2O) is not caused by any single compound but is rather due to many oxidation products having electron acceptor character. An analogy with ethereal solutions of chloro or nitro compounds may be noticed [1 - 6]. When the electron affinity is high enough PC can occur even in non-degassed solutions, provided the concentration of the acceptor is also sufficient [9].

The linear dependence of the rate constant of PC relaxation on the d.c. voltage applied between the electrodes provides evidence that photo-produced ions are discharged electrochemically on electrodes to neutral products since the process is quite reproducible. The rate of relaxation is limited by the transport of ions in an electric field. The slope of the $k = f(V)$ line may be roughly interpreted as μ/l^2, where μ is the mean mobility of ions and l is the space between the electrodes. The estimated values of μ are

typical for ions (about 10^{-4} cm^2 V^{-1} s^{-1}) and are supported by the method adopted for assaying ion mobilities in dielectric liquids [31, 32].

The bulk recombination process is probably preceded by a slow unimolecular or pseudounimolecular rearrangement, as this disappearance is also well described by the first-order rate equation.

The differences in the PCs of degassed THF, Et$_2$O and 1,4-dioxane are also worth considering. It is known that 1,4-dioxane undergoes oxidation and photo-oxidation, which can lead to similar products such as those formed in THF and Et$_2$O [15, 16]. However, PC signals for 1,4-dioxane were hardly detectable. A comparison of the parameters describing the physicochemical properties of these ethers reveals that the differences do not affect the parameters associated with spectral features. Considering their solvent properties, the studied ethers are very similar. Nevertheless, the PC behaviour is different. Thus, the very significant gap between the dark conductivities for THF, Et$_2$O and 1,4-dioxane, being respectively about 3×10^{-10} Ω^{-1} cm^{-1}, 5×10^{-13} Ω^{-1} cm^{-1} and 3×10^{-15} Ω^{-1} cm^{-1}, and the PC yields can be explained by the different polarities expressed by the electric permittivities and dipole moments. The PC must be profoundly affected by a polarity change. The lack of PC in 1,4-dioxane might be interpreted in this way. In 1,4-dioxane ion pairs are probably also photoproduced, but do not dissociate to free ions contributing to the d.c. PC. Also, the nature of the predissociation states might be partly responsible, and this aspect is being investigated in a more chemically defined system with known electron acceptors and will be published later.

The stability or resistance of these ethers to oxidation is clearly associated with their polarity. Thus, the rate of product formation in well-purified solvents monitored as the number and intensity of peaks on GC diagrams increases in the order of polarity of the solvents: 1,4-dioxane < Et$_2$O < THF. The THF and Et$_2$O had to be used practically immediately after distillation over reducing agents. Ethers could only be stored for longer times in degassed glass bulbs sealed under vacuum and kept in darkness in agreement with the conclusion reached by other investigators [18].

The contribution of polar processes resulting in stable ions as well as the considerable influence of polarity on PC and the stability of ethers may indicate that the polar paths of oxidation reactions, besides the commonly considered radical paths [16], are also very important channels in the chemistry of ethers.

The influence of air oxygen on the PC of ethers is crucial and interesting. The dark conductivity of degassed and non-degassed ethers was almost the same. Hence, the participation of molecular oxygen in dark electrode reactions can be eliminated. If that were not true, ethers containing dissolved oxygen (at a relatively high concentration of about 3.9×10^{-3} M [33]) should have exhibited higher dark conductivities. On the contrary, a not very significant but quite opposite effect was observed. A moderately polar aprotic environment and a rather small potential gradient on the electrode/solvent interface (d.c. voltage is mainly lost through ohmic resistance

of a liquid sample) do not promote the appearance of an oxygen reduction current such as that of the polarographic oxygen reduction wave.

None of the samples of the ethers purified in different ways showed PC when dissolved oxygen was present. Atmospheric pressure was enough to achieve an oxygen concentration which almost completely quenched the PC process. The first assumption was that oxygen takes part in photochemical reactions, for example, through the reactions

$$Et_2O + Y + h\nu \longrightarrow Et_2O^+ + Y^-$$

$$Y^- + O_2 \longrightarrow Y + O_2^-$$

$$O_2^- + Et_2O^+ \longrightarrow Et_2O + Y$$
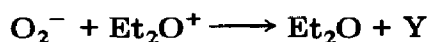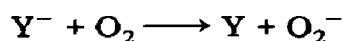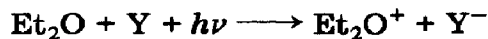
In such a case there should have been a clear short-lived relaxation component which should have disappeared after the degassing of a sample. However, such behaviour was not detected, so it seems that the mechanism is based rather on the quenching influence of oxygen on the predissociation states, whatever character they may have. In many investigations it is reported that oxygen causes a decrease in photocurrent yields owing to interaction with triplet states (for example, see refs. 4, 8 and 10). Thus, it is very likely that triplet states occur in the history of conversions leading to ionic photodissociation resulting in free ions.

By analogy with our studies on the PC of stronger electron acceptors such as aromatic nitrobenzenes in ethers [24], the PC in degassed ethers is due to photoelectron transfer between ethers as n donors and the impurity acceptor (Y). Photogenerated ions are fairly stable and behave as described. Smaller ions such as H^+, which could be responsible for a faster relaxation component, should not be excluded.

In conclusion, this work shows that the PC of degassed THF and Et_2O may be an additional criterion of their purity level. Present investigations also indicate the importance of polar paths of reactions of ethers in their oxidation and photo-oxidation processes.

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