

Studies on Ionic Solutions in Diethyl Ether

V. Redox Titration of Positive Triphenylmethyl Ion with Negative Triphenylmethyl Ion

CHRISTINA MANNERSKANTZ and LARS GUNNAR SILLÉN

*Department of Inorganic Chemistry, Royal Institute of Technology,
Stockholm, Sweden*

In the first three parts ¹⁻³ of this series ¹⁻⁴, it was demonstrated that a solution of lithium perchlorate in diethyl ether can be used as an ionic medium for studying ionic equilibria in ether solutions. In solutions containing small amounts of silver or halogenide ions in LiClO₄-ether the activity factors proved to be practically constant so that one could measure ionic concentrations directly, using emf measurements, and use concentrations instead of activities in the law of mass action. Among other things it proved possible ^{2,3} to calculate the solubility products of the silver halogenides and the complexity product of AgI₂.

We have now tried to use this ionic medium to study the reaction between triphenylmethyl perchlorate (R⁺ClO₄⁻) and lithium triphenylmethyl (Li⁺R⁻)^{*}. There is much evidence for the existence of the ions, R⁺ and R⁻, in solutions of these substances ⁵, and they are likely to react forming R (triphenylmethyl radical) or R₂ (hexaphenylethane). Bent's and Keevil's experiments with cells of the type

Na-Hg/Na⁺R⁻ in ether/Na⁺R⁻ in ether, saturated with solid R₂/Pt

indicated that steady potentials can be obtained with redox solutions containing R₂ and R⁻. One could expect that the redox potential during a titration of R⁺ with R⁻ would lead to curves with at least two "shelves": one with mainly R⁺ and R, one with mainly R and R⁻.

When in the following we use a symbol such as R⁻, this includes all sorts of complexes that R⁻ can form with the 2 C LiClO₄-diethyl ether medium; for instance molecules LiR and ether complexes.

Our experiments showed that the redox potentials were not as reproducible as those found with Ag⁺ and halogenide ions. In these experiments, considerable difficulties were met with because of impurities; the various forms of

* In the following, R = (C₆H₅)₃C (triphenylmethyl or trityl).

triphenylmethyl, especially R^- , are very sensitive to the decomposition products of $LiClO_4$ -ether, even if the latter is stored without access to oxygen or water.

With the procedure finally adopted, we have found evidence for the formation of an intermediate step, possibly R_2^- , in addition to R (or R_2) and have also been able to calculate the order of magnitude of the various equilibrium constants involved.

MATERIALS

Preparation of $LiClO_4$ (cf. Gmelin ⁷). In a 1 l flask, 300 g Li_2CO_3 (Kebo puriss.) was treated with 500 ml 70 % $HClO_4$ (p. a.). Most of the water was evaporated (preferably *in vacuo*) on a hot plate, the temperature of which should not exceed 150° C. The $LiClO_4$ was then recrystallized from 96 % ethanol. It was dried very carefully in an open porcelain dish at 60° C overnight, then ground in a mortar and dried for a few more hours at the same temperature. It should be well protected from dust and organic impurities to prevent decomposition during the later treatment at higher temperatures.

When the $LiClO_4$ did not smell of alcohol any more, it was recrystallized from water, sucked off on a glass filter plate, and redissolved in about 1 l water. The aqueous solution was filtered through a G 3 glass filter, and half of it was transferred to a 1 l Pyrex flask (Fig. 1 a). The flask was put into a vertical oven and the water evaporated under reduced pressure (water pump) at a temperature of 100–150° C. When almost all of the water was gone, the temperature was raised to about 200° C for one day. Next day it was kept around 230° C and then the $LiClO_4$ was melted by keeping the oven for one day at 260–270° C. The contents of the flask were kept at water pump pressure during the whole of this procedure. The temperature should never exceed 300° C.

Then an oil pump was connected and the melt kept at 1 mm Hg for at least half a day. Finally a stream of dry nitrogen was passed through the flask for a few hours, after which the melt should be allowed to cool in nitrogen. The dried salt can be kept in a closed vessel for one or two days but should preferably be used as soon as possible.

All of the ether used was distilled from sodium metal.

The nitrogen was taken from a cylinder and dried with dehydrite. The traces of oxygen were generally first removed with activated copper; always in work with Li^+R^- solutions.

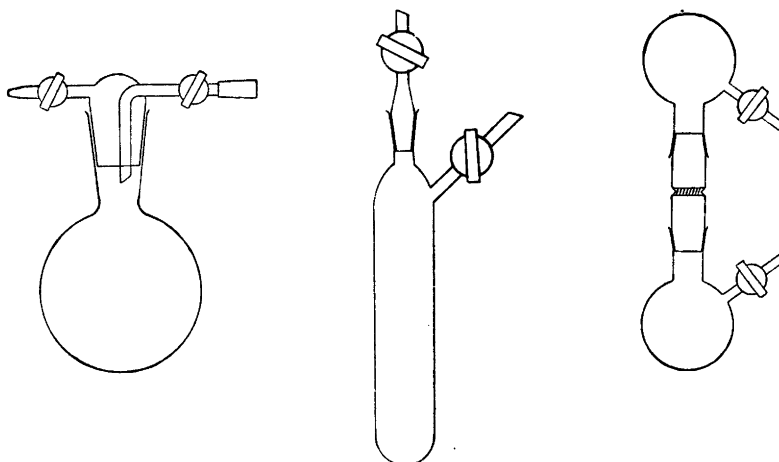


Fig. 1. a) Flask for drying $LiClO_4$ and preparing $LiClO_4$ -ether solution. b) Flask for preparing and storing $LiR-LiClO_4$ -ether solution. c) Apparatus for preparing and drying $LiClO_4$. Between the two flasks a G3 sintered glass filter is inserted.

Preparation and analysis of the LiClO₄-ether solution. When the flask was cool, it was fitted into a distillation apparatus and ether was distilled directly into the flask. The air was kept out of all vessels, if necessary by means of nitrogen, during this and all the following mixing operations. First the flask was rinsed with three portions of 50–100 ml ether. This ether was discarded after having dissolved the surface layer of the melt and all of the small drops adhering to the flask.

Then 250–300 ml of ether was distilled into the vessel and allowed to dissolve some of the LiClO₄ for half an hour with rather frequent but careful swirling. By then the LiClO₄ solution was usually close to 2 C. Half of it was transferred to another flask which was closed with a ground joint stopper with a stopcock on it to permit the release of the ether overpressure.

All joints and stopcocks should be lubricated with ether-resistant grease, prepared from starch and glycerol³.

The other half of the solution was swirled frequently during one hour until it became very viscous, its concentration then being about 4 C. It was transferred to another vessel and the exact LiClO₄ concentration was determined for both solutions with the ion exchange method, described in part II².

The solutions should be used immediately after analysis.

The first rinsing removes most of the moisture as was shown by the following analysis. The concentration of water in the LiClO₄-ether solutions was determined by Johansson's⁸ modification of Karl Fischer's titration method; 25 ml 2.7 C LiClO₄ (discarded) from a rinsing consumed 1.0 ml of an I₂ solution, 1 ml of which corresponded to 1.7 mg H₂O (0.004 % H₂O) while 50 ml 3 C LiClO₄-ether from the following extraction of the melt needed 0.5 ml of the same I₂ solution (0.001 % H₂O).

No Cl⁻ could be detected with silver nitrate after adding water to the LiClO₄-ether.

Preparation of LiR. LiR was prepared according to v. Grosse⁹. Lithium amalgam was first prepared by mixing 140 g Hg and 0.7 g Li in a flask which had a ground-joint stopper and a side-tube, both with stopcocks. The flask was filled with nitrogen during the mixing procedure and then evacuated by the oil pump and kept at 110° C for 5 days with occasional and very careful swirling. Finally it was cooled to room temperature and nitrogen passed through.

Triphenylmethyl chloride had been prepared according to Organic syntheses¹⁰; its melting point was 111–112.5° C after recrystallisation from absolute ether. Trityl chloride (4.7 g) was dissolved in 140 ml of ether, freshly distilled from sodium. This solution was pipetted (through the stopcock on the stopper) into the flask containing the lithium amalgam.

The vessel was rinsed with nitrogen, closed and shaken, and the ether overpressure released. Most of the reaction took place within half an hour but the LiR concentration increased if the vessel was left for a week and had then attained a value of 20–25 mC (16–20 % yield). The side-tube of the flask was then carefully warmed so that a polythene tube could be slipped on to it. The polythene tube was connected to the side tube of a similar flask, into which the clear LiR-ether solution could be decanted in a nitrogen atmosphere.

The remainder of the R groups may have been present either as RH or in the red crystals — probably LiR etherate — observed in the solid residue. At any rate no unreacted RCl was left; after a careful decantation and hydrolysis with alkali, tests with AgNO₃ showed that no chloride was present.

Analysis of the LiR-ether solution. The concentration of LiR was determined using benzyl chloride in absolute ether, as proposed by Gilman and Haubein¹¹ for the analysis of lithium alkyls. The previous filtration of the lithium alkyl solution recommended by these authors must be omitted in the case of lithium triphenylmethyl which decomposes on filtration through a glass filter. If the liquid has been carefully decanted it should be clear.

Example: 5 ml of LiR-ether was mixed with about 20 ml of water. The LiOH set free required 1.40 ml of 94 mC HCl for neutralization. Another 5 ml of LiR-ether was first allowed to react with benzyl chloride and then hydrolyzed. It then needed 0.60 ml of 94 mC HCl, possibly due to suspended LiOR, Li₂O, or LiOH (*cf.*¹²). *Result:* [LiR] =

$$\frac{(1.40 - 0.60) \cdot 94}{5} = 15.4 \text{ mC.}$$

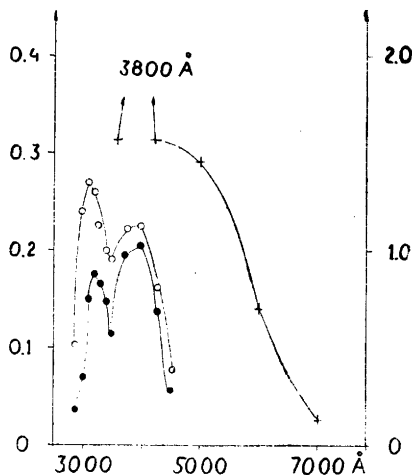


Fig. 2. Extinction curves for a) red-violet LiR-LiClO₄-ether solution (+, Fig. 3 c first point), bc) orange-colored solution from adding excess LiClO₄-ether to LiR-LiClO₄-ether (Fig. 3 c last point) and diluting with ether: b) protected from air (●), c) air blown through (○). The extinction scale to the right refers to a), that to the left to b) and c).

Preparation and analysis of the LiR-LiClO₄-ether solution. A certain amount of the solution of LiR in ether was mixed with sufficient of the stronger LiClO₄-ether solution to produce 50 ml solution of concentration equal to that of the weaker (about 2 C) LiClO₄ solution mentioned above. The vessel should permit only a small area of contact between the liquid and gas phase (Fig. 1b).

With solutions containing LiClO₄, we found that the benzyl chloride method for LiR gave either too high values or sometimes altogether anomalous ones. It was decided to try iodine titration instead: 5 ml LiR in LiClO₄-ether was pipetted into 5 ml of about 25 mC I₂ in ether. The excess of I₂ was removed with a slight excess of Na₂S₂O₃ and determined by back titration with an aqueous solution of I₂ using starch as indicator. Since the concentration of I₂ in ether changes rather quickly as the ether decomposes, the iodine solution should never be older than one day and a blank should be run.

Example: 5 ml of LiR-ether solution (same as in the previous example) was pipetted into 5 ml of a 23.6 mC I₂ solution in ether, the tip of the pipet being held under the surface. Reaction: I₂ + R⁻ → RI + I⁻. Excess (25 ml) of 10.2 mC Na₂S₂O₃ was added and titrated back with 4.08 mC I₂ in water; 21.8 ml was needed. A blank required 2.3 ml

$$4.08 \text{ mC I}_2. \text{ Result: } [\text{LiR}] = \frac{(21.8 - 2.3) \cdot 4.08}{5} = 15.9 \text{ mC.}$$

The following is an example of a remarkable behaviour. The concentration of a LiR-ether solution was determined as 20.7 mC by the benzyl chloride method. It was then diluted with LiClO₄-ether in the ratio of 4.75 : 10 so that the final concentration of LiR could be calculated to be 14 mC. When the benzyl chloride method was applied to this diluted solution, a higher value, 16.0 mC, was found.

When the LiR-ether solution mentioned above (15.4 mC by benzylchloride, 15.9 mC by I₂ method) was diluted with an equal volume of LiClO₄-ether (calculated 7.7 or 7.95 mC), 8.15 mC was found with the I₂ method.

The fact that the iodine method gives slightly higher values than the benzyl chloride method might be due to some uncharged R being present which would effect the I₂ consumption (2R + I₂ → 2RI) but not the consumption of acid. However, the behavior of the benzyl chloride method on dilution with LiClO₄-ether is unexplained.

At any rate, the I₂ method was given preference, since it was important, when a new emf titration was to be started, that the analysis for R⁻ in the LiR-LiClO₄-ether solution could be carried out quickly. In view of our analytical data we decided to subtract 10 % of the value obtained; the difference may have been due to R present, but we did not consider our data to allow an accurate correction.

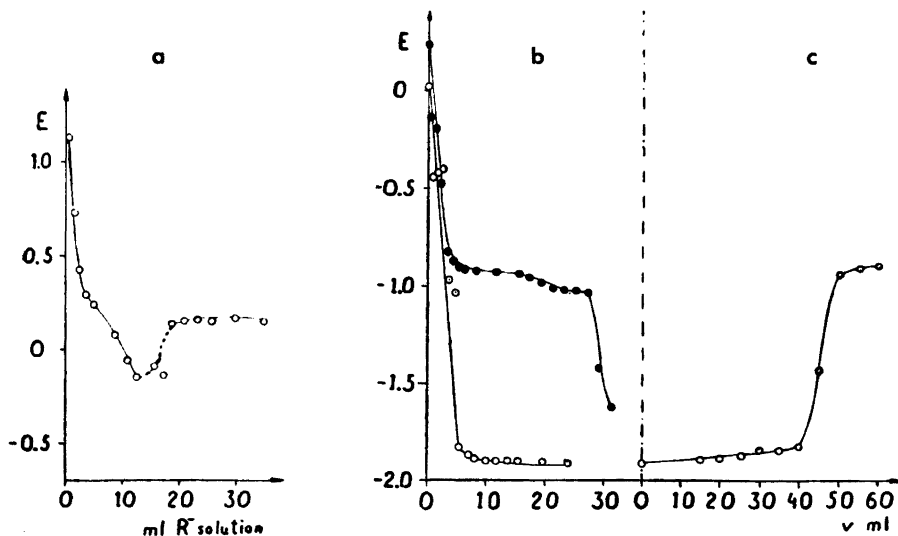


Fig. 3. Emf titration curves. a) R^- in ether was added to R^+ in 1 C $LiClO_4$ -ether with 0.03 % H_2O . b) Circles \circ , 7.7 mC R^- in ether was added to 10 ml 2 C $LiClO_4$ in ether less than one day old. Dots \bullet : 15.4 mC R^- was added to 10 ml 2 C $LiClO_4$ -ether 5 days old. c) To the final solution in Fig. 3 b was added 2 C $LiClO_4$ -ether one day old. — In all these experiments, old $LiBr-LiClO_4$ -ether was used in the reference electrode.

The LiR -ether solution is bright red and changes rather dramatically, on mixing with $LiClO_4$ -ether, to a deep red color with a violet tinge. We have made some preliminary studies on this latter solution with a Beckmann spectrophotometer (extinction curve, Fig. 2 a). Since LiR may decompose on dilution we used a Baly cell (Zeiss) with a very thin layer of the liquid, protected from air. As reference solution, $LiClO_4$ -ether was used. The cells should be put into water immediately afterwards, otherwise the separable parts will become inseparable.

Preparation of $RClO_4$. Solid $RClO_4$ was prepared according to Hofman and Kirmreuther¹² and was always used within three weeks. The products obtained by Gomborg and Cone's method¹³ were less pure, as seen from melting points and consumption of OH^- after hydrolysis.

1 g triphenyl carbinol was dissolved in 10 ml acetic anhydride, and the solution was cooled in an ice-salt bath to about -15 to $-17^\circ C$. While the solution was still clear, 1 ml 70 % $HClO_4$ was added and the yellow precipitate filtered off, washed with acetic anhydride and dried in a nitrogen atmosphere. It was left for two days in a desiccator over P_2O_5 and should then have a melting point of $140-141^\circ C$ which was not raised by recrystallization from acetic anhydride or nitrobenzene. The apparatus for filtering and drying $RClO_4$ is shown in Fig. 1 c.

When 435 mmole $RClO_4$ (as calculated from the weight) was hydrolyzed with about 50 ml water in an E-flask, 429 mmole acid (98.6 %) was found on titration with $NaOH$.

When the salt was dissolved in 2 C $LiClO_4$ -ether, a 1.3 mC solution was obtained which kept its yellow color for a few hours. When stored the salt was always kept over P_2O_5 . The color shifted slowly from deep yellow to dark brown when the salt was stored for a month or more.

The salt was decolorized on washing with ether which had been in direct contact with sodium metal and then sucked off instead of distilled. It seems likely that the cause was a small amount of $NaOH$ in the ether.

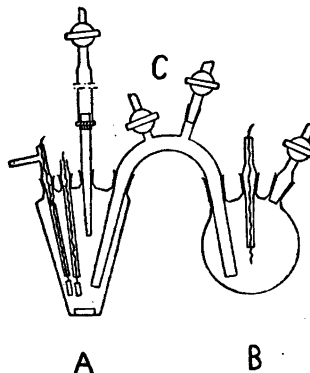


Fig. 4. A = Titration vessel with redox electrodes and stirrer. B = reference electrode vessel. C = salt bridge.

Preparation of LiBr solution. A good grade of LiBr (Kahlbaum, DABV) was dried for one day at 180° C under oil pump vacuum. Ether was distilled into the cooled flask and left in contact with the salt for a few days. The LiBr content was determined by the ion exchange method.

APPARATUS

The cell studied,



was kept in a thermostated room at 20° C \pm 1° C (the constancy was usually better than this). At higher temperatures, the vapor pressure of ether becomes inconveniently high.

In each titration there were two redox electrodes in the solution: a gold foil which had been ignited in a methanol flame and a palladinated Pt electrode prepared according to Hamer and Acree¹⁴. The Ag,AgBr electrode was prepared by Brown's method¹⁵ and, like the Pt electrode, was dried by dipping it into absolute ethanol and then into three successive baths of absolute ether just before use.

A Radiometer of type PHM 22 was used for measuring the emf.

The glass apparatus is shown in Fig. 4; A is the titration vessel with Au and Pd-Pt electrodes, buret, magnetic stirrer enclosed in polythene, and inlet for the liquid junction. The RClO₄ was introduced through an inlet on one side, closed with a ground-joint stopper. B is the reference electrode vessel containing the Ag,AgBr electrode and inlet for liquid junction whilst C is the liquid junction with stopcocks for venting the nitrogen. Nitrogen was let into the apparatus through one of the electrodes which had a sidetube on top and a hole rather high up to the hollow stem.

The buret. Since ordinary stopcocks did not stop ether leakage, we tried burets from which the ether solution was let out by means of a polythene tube containing a glass bead. A considerable force was required to squeeze the tube so that liquid ran out, but after some time of use leakage occurred between additions. We then began to use a buret with a Teflon screw outlet (Johns-Manville Products) which proved to be altogether ideal for ether solutions. The upper part of the buret was joined to a tube containing a stopcock. For filling the buret, a rubber suction bulb was attached to the tube and the LiR solution was sucked up through a polythene tube drawn out to a capillary of diameter about 1 mm. This polythene tube had been slipped over the tip of the buret so that it reached the bottom of the narrow storage vessel.

When the buret was to be attached to the titration vessel, part of the polythene tube was cut off with a pair of scissors. A short part of it was left which almost reached down into the liquid, thus avoiding a too long passage of the ether solution through the gas phase. Since LiR is quickly destroyed if allowed to stand in a thin-walled polythene vessel surrounded by air, the operation should be carried out quickly and the polythene tube kept down in the nitrogen atmosphere of the storage vessels as much as possible. The ground joint of the buret should fit into that of the storage vessel.

SOURCES OF ERROR

It was important that the LiBr-ether solution should not be more than one week old when used. Otherwise the emfs were quite different from those with fresh solutions. For instance, the E at the end of the redox titration (large excess of R^-) was about -1.20 V with fresh solutions but about -2.00 V with a six weeks old solution. The electrode potential of the reference half-cell did not change; it was found that the potential difference between an Ag,AgBr electrode in an old LiBr solution and a similar electrode in a new LiBr solution was at most only a few mV, as could also be expected from the results in part I—III¹⁻³.

Our only explanation is that degradation products of the ether solution move through the salt bridge to the titration vessel and affect the redox potentials there.

In the first fourteen titrations carried out, we ran into difficulties which were traced back to impurities in the LiClO_4 -ether solution. If the LiClO_4 melt was not dried under the oil pump vacuum, or if the first extract with ether was used, the water content of the LiClO_4 -ether was too high.

The influence of water is demonstrated by the curve, Fig. 3a, where R^+ in 1 C LiClO_4 -ether, containing 0.03 % water, was titrated with R^- in ether; it is quite unlike the curves obtained with less water present and using fresh solutions (Fig. 5).

The ionic strength was kept constant by always adding an equal volume of 2 C LiClO_4 -ether. The curves in Fig. 3b show the effect of time. In curve I (○), 7.7 mC LiR was added to 10 ml of LiClO_4 -ether, containing only 0.001 % H_2O and less than one day old. In curve II (●), 15.4 mC LiR in ether was added to 10 ml of the same 2 C LiClO_4 -ether which was now five days old. A considerable amount of impurities had obviously formed during this time interval.

The curve in Fig. 3c was obtained when fresh LiClO_4 -ether solution was added to the final solution from 3b, curve I. When the violet red LiR- LiClO_4 -ether solution (extinction curve in Fig. 2a) had been decolorized, the solution at first turned light yellow, and after a few minutes the yellow color changed to orange, a color which disappeared if the solution was exposed to air. Extinction curves were taken up of this orange colored solution, after diluting 26 times with ether; the solution was protected from air in an ordinary quartz cuvette with a ground stopper, Fig. 2b. The same solution was also studied after exposure to air, extinction curve 2c. As reference solution a very weak LiClO_4 -ether solution was used; for wavelengths less than 2 900 Å the reference solution had the larger extinction.

A maximum at 4 000 Å is present in all three curves, but only the violet red solution from Fig. 2a absorbs in the region 5 000—7 000 Å. As mentioned already a Baly cuvette was used, difficulties were met with when using ordinary cuvettes since it is necessary to dilute the solutions to avoid too large absorption, and the dilution may destroy most of the sensitive compounds.

FINAL PROCEDURE

Since the LiClO_4 -ether solutions proved to decompose even without access to air and moisture, it was imperative to use fresh solutions and to work quickly. The elaborate technique for keeping air and moisture away that proved useful in the work with $\text{Ag}^+ - \text{I}^-$ (part III) would here have been unwieldy and had meant a great waste of chemicals; in our work with triphenylmethyl no "stock solution" could be stored even for a week. The procedures we used were compromises between the fear of contamination from the air and the urge for quick work.

Before a titration was started, the apparatus was filled with nitrogen, and the reference electrode vessel charged with 50 ml of a solution (2 C LiClO_4 , 0.1 C LiBr). Into the titration vessel, 5–10 ml 2 C LiClO_4 -ether was pipetted, and the liquid junction was filled with the same solution. Then LiR in 2 C LiClO_4 -ether was added from the buret. A few ml of LiR were always destroyed by various impurities: by traces of moisture and oxygen adhering to the electrodes, to the sintered glass-plate of the liquid junction or to the glass walls, or by impurities in the ether originally present in the titration vessel or in the ether flowing down from the liquid junction. We could not remove such impurities altogether, and it was hard to reduce the initial consumption of LiR even to its present size. When the impurities had reacted and a small excess of R^- began to appear, the solution turned red and E attained a value of about -1.2 V.

At this point a weighed amount of RClO_4 was carefully introduced. The color changed immediately to light yellow, and E changed to about 0.3 V. Now the main part of the titration was started: LiR was added, about 1 ml at a time until the solution after an intermediate region of dark yellow to greenish brown turned red again and E had decreased again to about -1.2 V.

The gold electrode and Pd-Pt electrode finally attained the same value; the gold electrode gave the final emf almost immediately, the Pd-Pt electrode after 5 minutes – 1 hour. In a solution containing excess LiR , the delay was rather small.

Typical E curves are shown in Fig. 5 and will be discussed below. At the second sharp drop the initial red color disappeared again after about 2 minutes; with 1 ml excess of LiR the red color remained for about 5 min, and if 1 ml more of LiR was added the color kept for almost one hour. On the other hand, red drops adhering to the buret might keep their color for up to about an hour. This indicates that R^- reacted with a component of the solution and not with a component of the gas phase especially as the contact area between liquid and gas phase rather increased slightly due to the shape of the titration vessel.

It is best to maintain a very small overpressure of nitrogen in the vessel. The solutions should be kept in the dark as much as possible.

The final reaction in which LiR is destroyed is so slow that it has been difficult to investigate it.

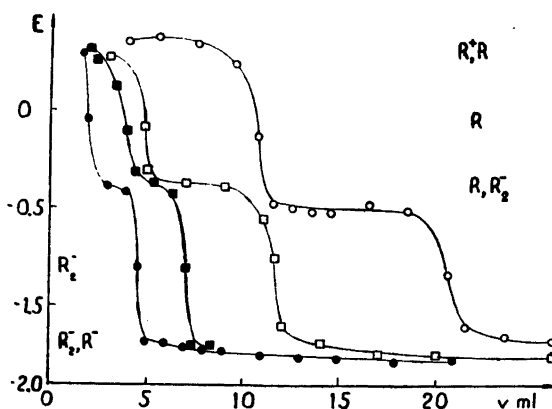


Fig. 5. Reproducible curves obtained with purified materials. Amount of $RClO_4$ added: ● 4.8, ■ 5.3, □ 5.4, ○ 14.4 mg. The curves are shifted slightly sideways, so that the total volume of the solutions was, in the order mentioned, $9.4 + v$, $10.7 + v$, $10.2 + v$ and $11 + v$ ml. We have assumed that the first equivalence point (R_1^-) was at 1.9, 3.9, 4.8, and 10.67 ml, and the second (R_2^-) at 4.5, 11.6, and 20.6 ml.

DISCUSSION OF THE CURVE

Fig. 5 shows typical curves. They have two equivalence points (sharp drops) and three "shelves". It seems reasonable that one of the equivalence points should correspond to the prevalence of the uncharged form R (or R_2) in the solution. From the concentrations of the solutions it was quite clear that this must be the first equivalence point.

In these titrations we knew the amount of R^+ added, and also approximately the concentration of the R^- solutions. However, it was hard to determine exactly the excess of the R^- after destroying the impurities; so this excess was calculated by assuming the first sharp drop to correspond to the completion of the reaction:

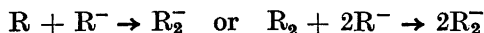


The second sharp drop might be due to one of two possible causes. Either R^- reacts with the products formed when R^- previously reacted with the impurities (which may now also have reacted with R^+), or R^- reacts with R (or R_2). Table 1 shows that the amount of R^- consumed between the two equilibrium points has no relation to the amount needed for the destruction of the impurities but is almost equal to the amount of R formed at the first equilibrium point (twice the amount of R^+ added).

Table 1.

Mole R^- for impurities	Mole R formed	Mole R^- used betw. eq. points	R^- betw. eq. points R^- for impurities	R^- betw. eq. points R formed
69.3	84.0	88.2	1.27	1.05
38.9	31.5	57.6	1.48	1.83
112.8	30.9	37.7	0.33	1.22
103.0	28.0	33.4	0.32	1.19

If the differences between the benzyl chloride and iodine analyses for R^- are ascribed to R present in the R^- solutions, the ratio will be still closer to 1. This indicates that we have a reaction:



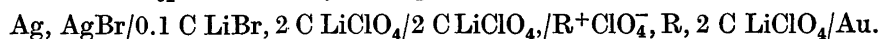
One reason why the ratio in the last column of Table 1 may come out somewhat higher than 1 is that the LiR solution is very sensitive and may be destroyed to a slight extent in the course of the titration. So, in the following calculations, we have recalculated the concentration of R^- using the amount of $R^+ClO_4^-$ weighed in, and the volume of R^- solution consumed between the two sharp drops, assuming them to correspond to the compositions R and R_2^- .

CALCULATION OF EQUILIBRIUM CONSTANTS

If we assume that R^+ , R , R_2^- and R^- are the main forms of triphenylmethyl present during the titration, we may calculate from the data in Fig. 5 three "molar potentials" E_{01} , E_{02} , and E_{03} :

Symbol	$E_{01}(R^+ + e^- \rightarrow R)$,	$E_{02}(2R + e^- \rightarrow R_2^-)$,	$E_{03}(R_2^- + e^- \rightarrow 2R^-)$
●	0.32	-0.18 - 0.22 - 0.18	-1.38 - 1.38 - 1.38 - 1.37 -1.37 - 1.38 - 1.37 - 1.37 -1.37
■	(0.16)	-0.20 - 0.20 - 0.19	(-1.48) - 1.40
□	0.32	-0.23 - 0.22 - 0.19(-0.26)	-1.41 - 1.43 - 1.42 - 1.41 -1.39
○	0.30 0.36	-0.38 - 0.38 - 0.37 -0.29 - 0.28	-1.36 - 1.34 - 1.32 - 1.31 -1.31

For instance, E_{01} is defined by the equation, for the emf of a cell:



$$E = E_{01} + \frac{RT}{F} \ln \frac{[R^+]}{[R]} = E_{01} + 0.058 \log \frac{[R^+]}{[R]} \quad (2)$$

The reference half-cell is thus always $Ag, AgBr/0.1 \text{ C } Br^-$ in $2 \text{ C } LiClO_4$. The experimental accuracy would make it meaningless to give the figures with a higher accuracy than 0.01 V.

Values within brackets have been disregarded, usually because the points were close to an equivalence point so that the concentrations were not known with sufficient accuracy.

Disregarding one of the titrations (○) which deviates somewhat from the others, we shall use the following tentative values:

$$\begin{aligned} R^+ + e^- &\rightarrow R; & E_{01} &= 0.32 \pm 0.05 \\ 2R + e^- &\rightarrow R_2^-; & E_{02} &= -0.23 \pm 0.05 \\ R_2^- + e^- &\rightarrow 2R^-; & E_{03} &= -1.40 \pm 0.03 \end{aligned} \quad (3)$$

From these E_0 values one may calculate the equilibrium constants for a few reactions of interest

$$\begin{aligned}
 \text{R}^+ + \text{R}_2^- &\rightleftharpoons 3\text{R}; \quad \log K = \frac{E_{01} - E_{02}}{0.058} = 9.5 \pm 1.5 \\
 \text{R} + \text{R}^- &\rightleftharpoons \text{R}_2^-; \quad \log K = \frac{E_{02} - E_{03}}{2 \cdot 0.058} = 10 \pm 1 \\
 \text{R}^+ + \text{R}^- &\rightleftharpoons 2\text{R}; \quad \log K = \frac{2E_{01} - E_{02} - E_{03}}{2 \cdot 0.058} = 19.5 \pm 1.5 \\
 \text{R}^+ + 3\text{R}^- &\rightleftharpoons 2\text{R}_2^-; \quad \log K = \frac{2E_{01} + E_{02} - 3E_{03}}{2 \cdot 0.058} = 39.5 \pm 3
 \end{aligned} \tag{4}$$

If, on the other hand, one assumes R_2 to predominate over R , E_{01} and E_{02} are replaced by E'_{01} and E'_{02} :

Symbol	E'_{01} ($2\text{R}^+ + 2\text{e}^- \rightarrow \text{R}_2$)	E'_{02} ($\text{R}_2 + \text{e}^- \rightarrow \text{R}_2^-$)
●	0.39	-0.32 - 0.37 - 0.36
■	(0.23)	-0.34 - 0.35 - 0.37
□	0.38	(-0.37) - 0.37 - 0.36 (-0.47)
○	0.43 0.36	-0.51 - 0.52 - 0.51 - 0.44 - 0.45

We shall use the following tentative values:

$$\begin{aligned}
 2\text{R}^+ + 2\text{e}^- &\rightarrow \text{R}_2; \quad E'_{01} = 0.39 \pm 0.05 \\
 \text{R}_2 + \text{e}^- &\rightarrow \text{R}_2^-; \quad E'_{02} = -0.36 \pm 0.03 \\
 \text{R}_2^- + \text{e}^- &\rightarrow 2\text{R}^-; \quad E_{03} = -1.40 \pm 0.03
 \end{aligned} \tag{5}$$

The equilibrium constants will then take the following form:

$$\begin{aligned}
 2\text{R}^+ + 2\text{R}_2^- &= 3\text{R}_2; \quad \log K = \frac{E'_{01} - E'_{02}}{\frac{1}{2} \cdot 0.058} = 26 \pm 2 \\
 \text{R}_2 + 2\text{R} &= 2\text{R}_2^-; \quad \log K = \frac{E'_{02} - E_{03}}{0.058} = 18 \pm 1 \\
 \text{R}^+ + \text{R}^- &= \text{R}_2; \quad \log K = \frac{2E'_{01} - E'_{02} - E_{03}}{2 \cdot 0.058} = 22 \pm 1 \\
 \text{R}^+ + 3\text{R}^- &= 2\text{R}_2^-; \quad \log K = \frac{2E'_{01} + E'_{02} - 3E_{03}}{2 \cdot 0.058} = 40 \pm 1
 \end{aligned} \tag{6}$$

Since the dissociation constant of R_2 in many solvents seems to be of the order of magnitude 10^{-4} (see Waters¹⁶) and the concentration of R or R_2 in the solutions is of the order 10^{-3} to 10^{-4} it is not possible to tell a priori which of the two forms will predominate in our LiClO_4 -ether solutions. If our emf data had been more accurate, one might have drawn some conclusions from the shapes of the two first shelves; as it is, we have to leave the question open.

SUMMARY

Using 2 C LiClO_4 -ether as ionic medium, potentiometric (redox) titrations have been made of the positive triphenylmethyl ion, R^+ , with the negative triphenylmethyl ion, R^- ($\text{R} = (\text{C}_6\text{H}_5)_3\text{C}$). The emf curves show two sharp

drops which can be explained in terms of the formation of $R(R_2)$ and a complex, R_2 . The equilibrium constants for the various reactions between R^+ , $R(R_2)$, R_3 and R^- in this medium have been estimated, (4) and (6). — The work was complicated by the fact that the redox potentials were very much influenced by the decomposition products of $LiClO_4$ -ether, which are formed rather rapidly but did not disturb previous work with Ag^+ and halogenide ions in the same ionic medium.

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REFERENCES

1. Part I: Berglund, U. and Sillén, L. G. *Acta Chem. Scand.* **2** (1948) 116.
2. Part II: Ålin, B., Wåhlin, E. and Sillén, L. G. *Acta Chem. Scand.* **3** (1949) 321.
3. Part III: Ålin, B., Evers, L. and Sillén, L. G. *Acta Chem. Scand.* **6** (1952) 759.
4. Part IV: Ekelin, K. and Sillén, L. G. *Acta Chem. Scand.* **7** (1953) 987.
5. Hammett, L. P. *Physical organic chemistry*, New York 1940, pp. 55 and 49.
6. Bent, H. E. and Keevil, N. B. *J. Am. Chem. Soc.* **58** (1936) 1228; Keevil, N. B. *Ibid.* **59** (1937) 2104.
7. Gmelins Handbuch der anorg. Chemie, 8. Edition **20** (Li)166.
8. Johansson, A. *Svensk Papperstidn.* **50** (1947) 124.
9. v. Grosse, A. *Ber.* **59** (1926) 2652.
10. *Org. Syntheses* **23** (1943) 100.
11. Gilman, H. and Haubein, A. H. *J. Am. Chem. Soc.* **66** (1944) 1515.
12. Hofmann, K. A. and Kirmreuther, H. *Ber.* **42** (1909) 4861.
13. Gomberg, H. and Cone, L. H. *Ann.* **370** (1909) 194.
14. Hamer, W. J. and Acree, S. F. *J. Res. Natl. Bur. Standards* **33** (1944) 87.
15. Brown, A. S. *J. Am. Chem. Soc.* **56** (1934) 646.
16. Waters, W. A. *Chemistry of free radicals*, Oxford 1948, p. 54.

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