stants is as good as could be expected in the case of the methylhexanes. The discrepancy in the case of the dimethylpentanes amounts to about 1000 cal. in terms of ΔF°.

To within the accuracy of the data, the values of ΔF° for the methylhexane reaction are representable by $\Delta H^\circ = -436$ cal. and $\Delta S^\circ = +0.55$ cal./deg. Standard states are the pure liquids. The rate of change of ΔF° is rather large in the case of the dimethylpentanes. We do not have results at sufficiently closely spaced temperature intervals to permit an accurate computation of ΔH° and ΔS°, ΔS° changes sign in the vicinity of 0° at which temperature, ΔH° has a value of about -475 cal.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYRACUSE UNIVERSITY]

The Identification of Solvated Electrons and Radicals in Rigid Solutions of Photoöxidized Organic Molecules; Recombination Luminescence in Organic Phosphors[1]

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Rigid solutions of alkali metals in solvents containing methylamine show an absorption peak at 6000 Å. Upon illumination, a new band appears in the near infrared while the 6000 Å. peak diminishes. The new band is attributed to incompletely solvated electrons. This same infrared band is found in illuminated rigid solutions of easily oxidized organic molecules, indicating, in agreement with previous work of Lewis and Lipkin, that photo-ejection of electrons has occurred. Upon slight softening of the solvent, solutions of such organic molecules frequently emit light (delayed luminescence). This luminescence can be maintained for hours if the solvent viscosity is properly controlled. The phenomenon is quite general and occurs in a wide variety of molecules. Evidence is presented which establishes that the luminescence is due to triplet states arising from recombination of radicals and trapped or solvated electrons, both formed originally by photoöxidation of the parent molecule.

Among the key problems in photo-chemistry and radiation chemistry is the identification of high-energy intermediates formed during the reaction. The use of rigid or glassy solvents affords a good method for stabilizing labile products since such bimolecular processes as ion or radical recombination or dismutation may be prevented, and the unstable species studied by appropriate means. In a glass at low temperature, quenching of electronic energy by "internal conversion" to the ground state is also impeded[2,3] making it possible to identify metastable excited states by their luminescence[3,4] or even by their absorption.[3,5] The usefulness of rigid solvent techniques in studying the photochemistry and spectroscopy of complex molecules has been most clearly brought out in the beautiful work of G. N. Lewis and his school[3,4,6,7] in which a variety of photo-processes (triplet-state excitation, electron-ejection, bond dissociation) were established and studied by this means. Some peculiar luminescence effects also were observed, in addition to the well-known "normal" phosphorescence, due to triplet-singlet transitions.[8] Lewis and Bigeleisen[9] found extremely long afterglows ($\tau \sim 1$ hr.) in rigid solutions of N-lithium carbazole or diphenylamide. When the phosphor was withdrawn from the Dewar and allowed to warm up, the luminescence intensity increased many-fold, went through a maximum and finally died out as the solvent fully liquefied.[10] The work described in this paper was begun in order to extend previous studies on photo-processes in rigid solvents and, in particular, to clarify the mechanism of the "delayed luminescence" found by Bigeleisen.

The lifetime of this luminescence at liquid nitrogen temperature is far too long to be accounted for by a triplet–singlet transition of the type usually responsible for phosphorescence of aromatic organic compounds.[8] The enhancement of intensity on softening of the solvent is also contrary to experience with other organic phosphors, in which loss of rigidity causes increased thermal degradation. Since no change in the natural radiative lifetime occurs, this can only result in a diminution of intensity. It appeared therefore that the delayed luminescence was due either to a new type of transition, which was very strongly vibration-coupled, or to some type of viscosity-dependent recombination process.[11]

In the same series of studies, Lewis and Lipkin[6] showed that the illumination of many easily oxidized organic molecules (amines, phenols, dyes, etc.) in rigid solvents leads to the appearance of absorption bands which correspond to the known free radicals or semiquinones of these molecules, prepared by ordinary chemical oxidation. They therefore proposed that direct photo-ionization (or oxidation) occurs in such cases

$$R \xrightarrow{h\nu} R^+ + e^-$$

In most instances softening of the solvent by warm-

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[1] This work is supported by grants from the U. S. Atomic Energy Commission (Contract No. AT(30-1)-820) and the U. S. Army Signal Corps (Contract No. DA-36-039 SC-15533). Material in this paper is taken in part from the doctoral thesis of M. G. Berry (Dept. of Chemistry, Syracuse University, September, 1951).

[2] J. Franck and R. Livingston, *J. Chem. Phys.*, **9**, 184 (1941).

[3] G. N. Lewis, D. Lipkin and T. T. Magel, THIS JOURNAL, **63**, 3005 (1941).

[4] G. N. Lewis and M. Kasha, *ibid.*, **66**, 2100 (1944).

[5] D. S. McClure, *J. Chem. Phys.*, **19**, 670 (1951).

[6] G. N. Lewis and D. Lipkin, THIS JOURNAL, **64**, 2801 (1942).

[7] G. N. Lewis and J. Bigeleisen, *ibid.*, **65**, 2419 (1943).

[8] M. Kasha, *Chem. Revs.*, **41**, 401 (1947).

[9] G. N. Lewis and J. Bigeleisen, THIS JOURNAL, **65**, 2424 (1943).

[10] J. Bigeleisen, personal communication.

[11] H. Linschitz and M. G. Berry, Abstracts, 119th meeting of the American Chemical Society, Cleveland, Ohio, April, 1951.

ing restored the spectrum of the original molecule, R.

Working in ether–isopentane or ether–isopentane–alcohol (EPA) solvents, Lewis and Lipkin could find no absorption which might be ascribed to the solvated or bound electron which presumably must exist in the excited glass. By making use of solvents containing amines of low molecular weight, in which alkali metals are soluble, and comparing the spectra of alkali metals and organic molecules in these solvents, we have been able to identify the absorption bands of both radicals (or radical–ions) *and* solvated electrons in the irradiated glass. The disappearance of both bands occurs simultaneously with the appearance of delayed luminescence, on warming. A survey of the occurrence of the delayed luminescence shows that the effect is most pronounced in those molecules which combine ease of oxidation with a strong normal (triplet–singlet) phosphorescence. Solvents which afford good traps or binding for electrons also enhance the effect. The spectrum of the delayed luminescence corresponds to that of the normal phosphorescence. On the basis of these findings, we attribute the emission to excitation of triplet states by recombination of radicals and electrons formed initially by photo-oxidation of the original molecule.[11] The recombination is, of course, viscosity dependent, and at liquid N_2 temperatures may be very slow. Debye and Edwards[12] have measured the kinetics of such very long-lived emissions and found that their decay data could be interpreted, in agreement with this view, as a second-order process, with a variable jump-distance for recombination.

Experimental

1. **Solvents.**—In order to help identify the absorption bands of electrons ejected from photoöxidized molecules, solvents were developed in which both alkali metals and the organic molecules being studied were soluble and which could also form clear non-cracking glasses at low temperatures. It is necessary to use complex mixtures (EPTM) to meet these requirements. Numerous combinations of ammonia with isopentane, ether and various amines were tried, but were all unsatisfactory due to crystallization of ammonia on cooling. The glassing solvents generally used were: EPT—ether, isopentane, triethylamine, 2:3:3 or 5:5:2; EPTM—ether, isopentane, triethylamine, methylamine, 2:3:3:2 or 2:3:3:1; EPA—ether, isopentane, ethanol, 8:3:5.[13] The proportions given in this list represent volume ratios at the temperature of a Dry Ice–ethanol-bath, in which the component liquids were measured. EPTM was used for work on the alkali metals and related experiments and EPT was a generally useful solvent for substances other than metals. When simply checking for existence of delayed luminescence, cracking of the solvent is not important and pure triethylamine (T) frequently sufficed.

In working with solutions of alkali metals, or of metallic methides, amides, etc., extreme care was necessary in drying and elimination of all oxidizing impurities from the solvents. Squibb ether (for anesthesia), distilled from sodium, was stored over calcium hydride and metallic lithium. Triethylamine (Matheson) was distilled from calcium hydride and stored over fresh hydride. Isopentane (Phillips, pure grade) was washed with sulfuric acid, distilled and stored over hydride. Oxygen was removed from the solvents on the vacuum line by trap-to-trap distillation and thorough evacuation of uncondensed gas. The purified, degassed solvents were kept in storage bulbs attached to the vacuum line through ground joints and closed by silicone-lubricated stopcocks. Tank methylamine (Matheson) or ammonia was deoxygenated and dried by condensing over potassium, and repeated cycles of freezing, pumping and thawing. The solution was kept in a Dry Ice–ethanol-bath and the amine removed as needed by condensing in a trap with liquid nitrogen. EPTM solvent was prepared on the line by distilling each of the components into a calibrated capillary measuring tube immersed in a Dry Ice–ethanol-bath. After measurement, the components were distilled into a suitable mixing or storage tube and finally into the absorption cell or test-tube containing the substance to be studied. The final test of EPTM purity was its ability to dissolve potassium triphenylmethide or lithium metal without rapid reaction.

2. **Preparation and Analysis of Samples.**—Solutions of compounds stable in air were prepared by placing small amounts of the purified substance in Pyrex tubes or Vycor–Pyrex graded seals, evacuating thoroughly on the line, distilling in the degassed, mixed solvent and sealing off. The various amine, phenol and hydrocarbon salts were all prepared on the line by treating alkali metal with the appropriate organic compound in liquid ammonia solution. Triphenylmethyl chloride was used in the preparation of potassium triphenylmethide and the lithium salts were made from the corresponding purified amines or phenols. A "windmill" with three arms, one of which carried the absorption cell, was used for these preparations. The purified organic compound was placed in one arm of the carefully dried windmill, together with excess metal (lithium wire or potassium chips). The windmill was immediately attached to the line, evacuated, ammonia condensed on the reagents and any material clinging to the walls washed down. The reaction was allowed to continue until a permanent blue color developed. From time to time evolved hydrogen was pumped away. In the case of lithium diphenylamide and N-lithium carbazole, the reaction mixture was allowed to stand for 2–3 hours, cooling as necessary to keep the pressure below atmospheric. Ammonia was then completely removed, pumping to take off the last traces, and solvent (ether or EPT) was distilled in. After agitation and standing at room temperature, the slurry was poured into the next arm of the windmill, allowed to settle and the solvent decanted back. The product was then repeatedly recrystallized and leached by distilling solvent onto it from the first arm, chilling and decanting back. Unreacted amine was thus removed leaving the purified salt behind. Using a little solvent, the purified material was then transferred into the absorption cell or luminescence tube by another 90° rotation of the windmill, and the transfer and recrystallizing solvent removed. The final mixed solvent for the measurement was then distilled into the windmill, first onto the crude reaction products, to remove any last traces of acidic or oxidizing impurities, and thence onto the purified salt. The tube or absorption cell was then sealed off. In the case of the salts of diphenylamine and carbazole, a large number of recrystallizations and leachings were necessary to rid the spectra of luminescence arising from traces of the free bases.

The metallo-organic solutions were analyzed by precipitating the free bases with water, evaporating to remove volatile amines (from the solvent) adding one ml. of water to the residue and titrating with dilute acid to the inflection point representing formation of carbonic acid, using a Beckman micro glass electrode.

Solutions of alkali metal were also prepared in the windmill. A bit of metal was cut under oil, rinsed in dry ligroin or ether and dropped into a small quantity of dry ether in the thoroughly dry windmill, which was then immediately placed on the line and evacuated. In the windmill the metal was again washed with ether by a series of decantations into the waste side-arm and distillations back onto the metal. With reasonable care, the metal remained bright after this treatment, and all traces of oil were removed. The wash ether was then pumped off, the metal dissolved in ammonia or methylamine and a small quantity of the solution, estimated to yield approximately the desired final concentration, was poured into the absorption cell, the windmill being chilled beforehand to prevent any warming and decomposition of the solution in this operation. The solvent was then pumped off, leaving the metal finely subdivided, the proper measured volume of methylamine was distilled in, the metal dissolved, the remaining measured solvent components finally added and the cell sealed off.

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(12) P. Debye and J. Edwards, *J. Chem Phys.*, **20**, 236 (1952).

(13) The proportions 5:5:2 used by Lewis and his co-workers frequently give a cloudy, brownish glass, apparently due to separation of isopentane, even when purified and dried solvents are used.

Although the metal solutions (especially potassium) were very unstable above Dry Ice temperature they could be kept indefinitely in liquid nitrogen. Before measurement, the sealed-off tube was transferred briefly to a Dry Ice–ethanol-bath, allowed to soften till all cracks in the glass healed, then withdrawn, quickly wiped dry, immediately placed in the low-temperature Beckman cell holder and refrozen. This procedure gave clear glasses with no frosting of the cell windows, and avoided serious decomposition.

After measurement, the tubes were opened and analyzed for total alkali metal. This was done by quick evaporation of the organic solvent in a stream of pure nitrogen, followed by addition of a measured volume of CO_2-free water and *p*H determination in a sealed Beckman micro glass electrode. In some cases, micro-titration was carried out using the Beckman electrode. This method clearly takes no account of possible amide formation and, accordingly, the metal concentrations are maximum values. The samples were kept cold, as far as possible, but some amide formation could not be avoided by the methods used.

3. **Spectra.**—Absorption spectra of rigid solutions at low temperature were measured in a specially modified Beckman Model DU spectrophotometer[14] using 6-mm. absorption cells. Emission spectra were taken on a Bausch and Lomb medium quartz spectrograph[15] using Kodak Type 103-D or J plates. A rotating can phosphoroscope, essentially similar to that described by Lewis and Kasha[4] was used to obtain the phosphorescence spectra. For this purpose the sample was kept immersed in liquid nitrogen, and excited by a G.E. AH-6 mercury arc. The spectra of the "delayed luminescence" was obtained by briefly exciting the sample in liquid nitrogen, waiting at least 30 seconds for the "normal" phosphorescence to decay and then allowing the tube, backed by a cylindrical parabolic reflector, to warm up directly in front of the spectrograph slit. From 50 to 200 such cycles were needed to obtain good plate blackening. The "delayed luminescence" spectra showing the clearest fine structure were obtained using EPT-5:5:2 as solvent. In the case of diphenylamine, the phosphorescence spectrum was also taken in EPA solvent. Several samples of this compound were used in obtaining the delayed luminescence spectrum to minimize photo-decomposition. Fluorescence spectra were also taken at liquid nitrogen temperature, using 2537 or 3650 Å. excitation.

Results and Discussion

I. Identification of Absorption Bands of Solvated Electrons in Rigid Solvents—Reversible Light-induced Transformations in Alkali Metal Spectra.—Figure 1 shows the spectrum of a typical rigid lithium solution, and the changes obtained upon illumination. Due to the instability of the solutions the results are not entirely reproducible, in detail. However, the general features of the absorption and the effects of light are sufficiently well marked to be established beyond doubt. The original spectra show intense peaks at 6000 Å. with a less strong, broad background absorption extending throughout the visible and near infrared.[16] Upon brief exposure to light the intensity of the main red peak diminishes markedly and the infrared absorption is correspondingly enhanced. No sign of a definite maximum in the new spectrum was found within the range of measurement. The new spectrum persists as long as the solution is kept rigid. When the glass is carefully softened by allowing the nitrogen to boil away, and then refrozen, the original spectrum is restored.

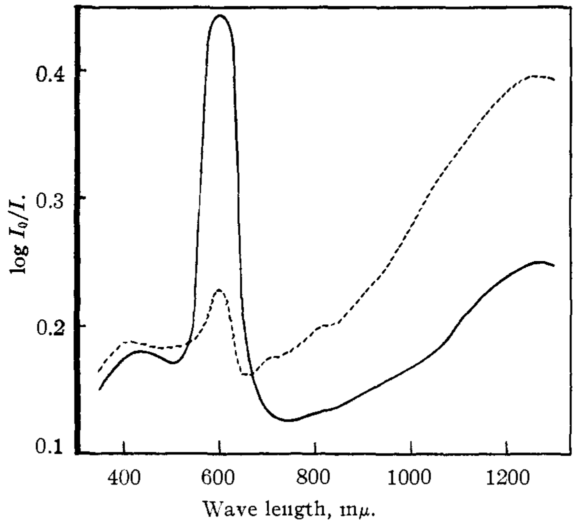

Fig. 1.—Reversible light-induced changes in absorption spectrum of rigid lithium–EPTM solution; total metal concentration, 8×10^{-5} *M*; solid line, original and final spectrum (after warming and refreezing irradiated glass); dashed line, after two-minute irradiation with AH-6 arc, through Corning filters No. 5113 and 3389 (4358 Å.); temperature, 78°K.

The solubility of potassium in EPTM, even containing maximum amounts of methylamine, is very much less than that of lithium, and the solutions are extremely difficult to work with because of their instability. Accordingly, no spectra are given. However, the fragmentary results obtained with this metal were in qualitative agreement with those for the lithium glass. The spectra show a band at 6000 Å. superimposed on a broad background absorption, illumination cuts down the 6000 Å. peak and enhances the infrared absorption, and thawing and refreezing restores the original spectrum.

Qualitative experiments using filters showed that the threshold for the light-induced transition is about 5400 Å., the 5461 Å. mercury line being barely effective while the 4358 Å. line caused an immediate change. No spectral changes were brought about by irradiation in the main red absorption band at 6000 Å.

It thus appears that solvated electrons, originally in a state giving rise to the 6000 Å. absorption may be transferred by light of higher energy into a new state with a broad absorption in the near infrared. Presumably, the effect arises as follows. In the original glass, prepared first as a liquid, the electrons are able to achieve maximum solvation energy by completely orienting solvent dipoles and are thus found in relatively deep traps. Upon excitation, these electrons are transferred to other regions of the glass where rigidity prevents dipole reorientation. The available traps are consequently less effective and absorption shifts toward the infrared. Softening the medium permits the electrons either to return to their original sites or to re-orient the dipoles in their neighborhood, restoring the original trap structure and spectrum. On this basis, one would expect to find that the absorption of electrons emitted by photoionization or oxidation of

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(14) Described in subsequent paper, p. 5839.

(15) We wish to thank Prof. N. Ginsburg of the Physics Department of Syracuse University for the use of both this instrument and his recording densitometer, and Mr. B. Harned for assistance in taking the densitometer tracings.

(16) In pure methylamine, G. E. Gibson and W. L. Argo, THIS JOURNAL, **40**, 1327 (1918), found the absorption maximum to lie at 6500 Å.

molecules in this glass would lie in the near infrared rather than in the 6000 Å. band.[17]

II. Absorption Spectra of Radicals and Electrons Formed by Photoöxidation of Organic Molecules.—Detailed studies were carried out on lithium diphenylamide and N-lithium carbazole, two substances which give especially brilliant delayed luminescence. Potassium triphenylmethide was also examined carefully since the spectrum of the free radical formed by electron ejection is known[18] and the behavior of this molecule helps establish the analogous processes in the other cases.

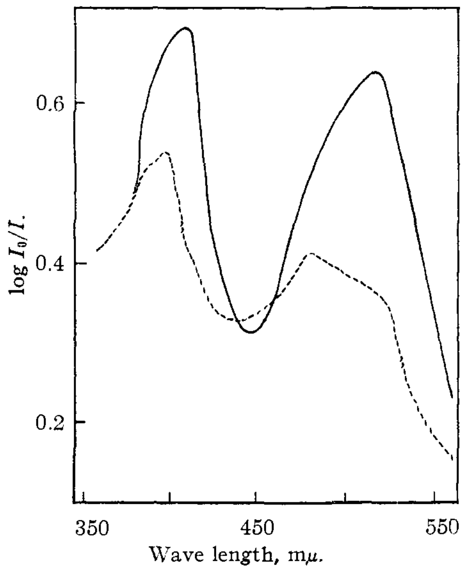

Fig. 2.—Effect of temperature on absorption spectrum of potassium triphenylmethide in EPTM; concentration, 6×10^{-4} M; dashed line, room temperature; solid line, 78°K.

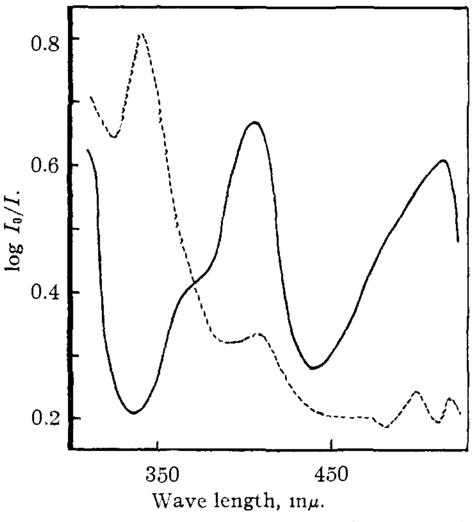

Fig. 3.—Photochemical formation of triphenylmethyl radical from triphenylmethide ion, in rigid EPTM solution; methide concentration, 6×10^{-4} M; solid line, original and final spectrum (after warming and refreezing irradiated solution); dashed line, after irradiation with AH-6 arc through Pyrex.

Solutions of potassium triphenylmethide in EPTM are somewhat unstable at room temperature, decomposing rapidly during the first few hours, with complete discharge of color after some weeks. Reaction presumably occurs between the strongly basic anion and methylamine. The solutions were therefore kept frozen as much as possible during handling. The effects of temperature and irradiation (AH-6 mercury arc, through Pyrex) on the absorption spectrum of the salt are shown in Figs. 2 and 3. We first note (Fig. 2) that cooling the solution from 300 to 90°K. intensifies the bands (the effects cannot be attributed simply to the relatively slight solvent contraction) and shifts the peaks to longer wave lengths. The shape of the room temperature curve strongly suggests the presence of a mixture of two forms of the ion. The results are in general agreement with Anderson's measurements at room temperature in ether solution except for the relative intensities of the peaks. Upon irradiation, the dotted curve of Fig. 3 is obtained, which is essentially identical with Anderson's curve for triphenylmethyl radical. The formation of the radical by photoöxidation of the anion is thus established. Softening of the solvent restores the original ion,

Experiments on a more concentrated methide solution (Fig. 4) enable one to observe relatively less intense bands developed in the near infrared upon irradiation. This band is similar to the very broad near infrared absorption observed in the rigid alkali metal glasses after illumination, and may therefore be ascribed to solvated electrons, photoejected from triphenylmethide ion and trapped in

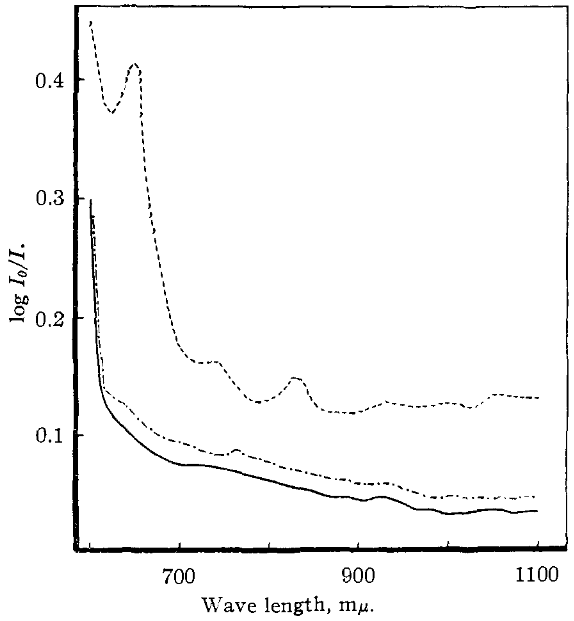

Fig. 4.—Enhanced near infrared absorption following illumination of potassium triphenylmethide in rigid EPTM solution; methide concentration, 8×10^{-3} M; solid line, original spectrum; dashed line, after irradiation with AH-6 arc; broken line, final spectrum (after warming and refreezing irradiated glass).

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[17] Further studies on the properties of solutions of alkali metals in *mixed* solvents will be published shortly. In this paper we present only such aspects of their behavior as are relevant to the problem of photo-ejection of electrons from organic molecules.

[18] L. C. Anderson, THIS JOURNAL, **57**, 1673 (1935).

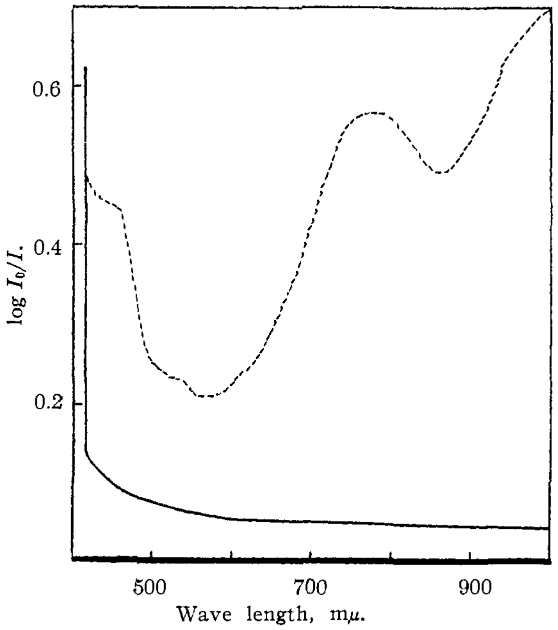

Fig. 5.—Reversible light-induced changes in absorption of lithium diphenylamide in rigid EPTM solution; concentration, 8 × 10^{-3} M; solid line, original and final spectrum (after warming and refreezing irradiated glass); dashed line, after irradiation with AH-6 arc.

disorganized regions of the medium. The low peaks at 6300, 7300 and 8200 Å. may be due to electrons in traps of various depths or possibly to oxidized or ionized photo-products other than triphenylmethyl.

Analogous reversible spectral changes in rigid solutions of lithium diphenylamide and N-lithium carbazole are presented in Figs. 5 and 6. In both cases the irradiated glass shows a broad band in the near infrared which we again attribute to the solvated electron. The band at 7500 Å., shown in Fig. 5, was obtained previously by Lewis and Lipkin[6] by the irradiation of various diphenylamine derivatives including lithium diphenylamide, and was ascribed by them to diphenyl nitrogen. In view of our results with triphenylmethide ion, this assignment is further substantiated. By analogy, the new peak at 6100 Å. in Fig. 6 presumably is due to the carbazole free radical, $(C_6H_4)_2N$.

It is possible that the electrons responsible for the infrared absorption may appear first in states corresponding to the 6000 Å. band, and that they are transferred out of this state by the same light that is used in the initial photo-ionization. The small peaks in the solvated electron bands of the densely colored triphenylmethide glass may thus be due to electrons permitted to remain in deep traps or to accumulate in specific types of traps because of the inner filter effect of the solute. However, as far as the identification of the electrons resulting from photo-ejection is concerned, this point causes no difficulty.

It is noteworthy that the presence of methylamine in the solvent, which is required in order to dissolve alkali metal (EPTM), is not necessary to obtain the infrared band which we associate with the incompletely solvated electron. Thus, a solution of lithium diphenylamide in rigid EPT solvent shows, upon irradiation, essentially the same spectral changes as in EPTM.

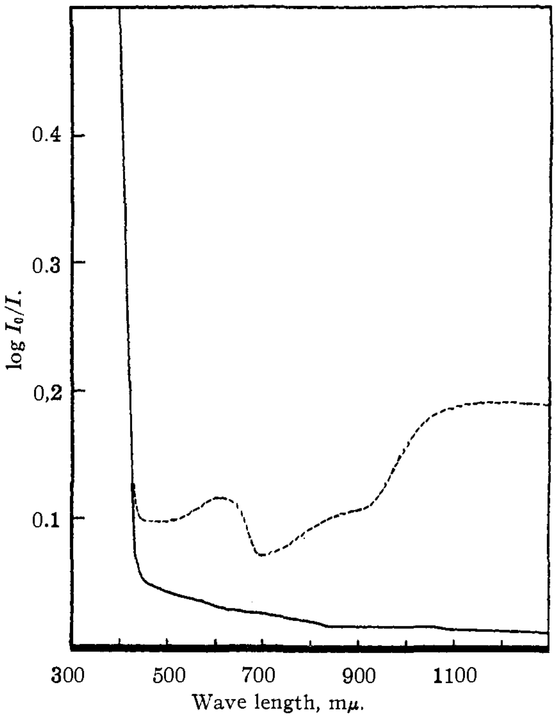

Fig. 6.—Reversible light-induced changes in absorption of N-lithium carbazole in rigid EPTM solution: solid line, original and final spectrum (after warming and refreezing irradiated glass); dashed line, after irradiation with AH-6 arc.

When an irradiated lithium diphenylamide glass is very slowly softened by allowing the nitrogen level to sink in the Dewar, the typical delayed luminescence appears. Reimmersion in nitrogen will quench the luminescence, so that the absorption may be measured at various stages of discharge of the "glow curve." It is found that the absorption bands of both the radical and solvated electron begin to fall simultaneously with the onset of luminescence. The drop in absorption parallels light emission until, finally, the radical and electron bands and luminescence all vanish together. This observation gives additional evidence for the recombination mechanism for delayed luminescence.

III. Spectra of Normal Phosphorescence and Delayed Luminescence.—Densitometer tracings of the phosphorescence and delayed emission spectra of N-lithium carbazole are presented in Fig. 7. It is apparent that the two types of emission are identical. Similar close correspondence was found for diphenylamine (peaks at 3995, 4175 and 4265 Å.[4] and lithium diphenylamide (main peak at 4770, shoulder at 5140 Å.). The delayed luminescence spectra show no visible trace of any radiation corresponding to the fluorescence emission of these substances. The correspondence between the phosphorescence and delayed luminescence spectra does not yet conclusively establish that the excited state responsible for the delayed luminescence is the triplet because what is usually regarded as "normal phosphorescence" may be combined with an un-

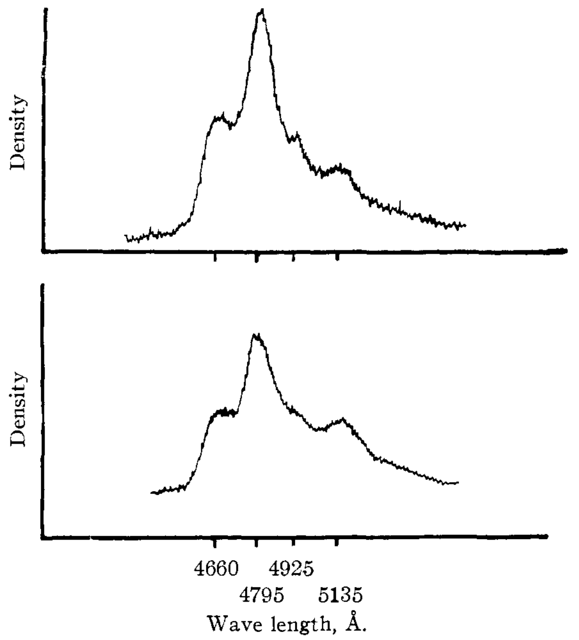

Fig. 7.—Spectra of N-lithium carbazole in EPT: upper curve, phosphorescence; lower curve, delayed luminescence; E. K. type 103-D plate; slit = 0.2 mm.

certain amount of recombination luminescence, even at liquid nitrogen temperature. This possibility is especially relevant in amine solvents, and in the case of the readily oxidized salts studied here. However, two experimental facts oppose this objection. First a relatively intense fluorescence spectrum was obtained for N-lithium carbazole, indicating that a large fraction of the excited molecules return to the ground state without ionization. It is reasonable to suppose that an appreciable fraction of excited molecules would also reach the triplet state without ionization. Second, the phosphorescence spectrum of diphenylamine taken either in EPA or EPT solution resembles the delayed luminescence spectrum in EPT. In EPA diphenylamine shows a very much weaker delayed luminescence than in EPT, and we may assume that the phosphorescence observed in the alcohol solvent is essentially "normal." We therefore conclude that the excited state responsible for the delayed luminescence is the lowest triplet. In all other cases (see "D" below) in which the delayed luminescence is sufficiently bright to obtain a good visual color judgment, agreement is also found between the two types of emission. In the case of the lithium salts, confusion in the visual correspondence may arise because of the difficulty of obtaining preparations of the salts completely free of the strongly luminescent parent amines.

Further evidence substantiating these conclusions comes from observations on glassy solutions of diphenylamine, which show a purple color during illumination.[6] This color disappears at the same rate as the normal phosphorescence and has accordingly been assigned to the triplet state itself. When an irradiated solution of diphenylamine is warmed to develop the delayed luminescence, the purple color appears very fleetingly, again indicating formation of the triplet upon recombination.

It is, of course, to be expected that radical–electron combination will result in the formation of triplets in good yield, but the absence of any singlet–singlet emission in the delayed luminescence spectrum is striking. The fact that intense fluorescence spectra were obtained for N-lithium carbazole[19] indicates that this is not due primarily to a high probability of radiationless transition from excited singlet to triplet. It seems more likely that the potential energy surface of the radical happens to lie closer to the triplet surface than to the excited singlet, so that capture would favor formation of the triplet.[20] Presumably, the electron, having fairly high mobility, may recombine with the radical while the solvent is still sufficiently rigid to protect the resulting high-energy triplet from thermal degradation by internal conversion.[3] Radiative return to the ground state may then occur. Such a mechanism suggests that the phenomenon of delayed luminescence should be most marked in those compounds which readily undergo photoöxidation and which have a strong normal phosphorescence. These expectations are borne out by experiment.

IV. Occurrence of Delayed Luminescence.—A representative number of compounds were examined in EPT or T. In the following list, rough visual estimates of the intensity of the effect are given as strong, medium, weak and very weak. It was found that the luminescence, first seen by Bigeleisen in the case of the diphenylamine salts, is a very widespread phenomenon.

Delayed luminescence was found in the following cases: lithium diphenylamide (s.), α-naphthylamide (s.), α-naphtholate (s.), α-naphthionate (v.w.); N-lithium carbazole (s.); potassium anilide (w.), phenolate (w.), triphenylmethide (m.); diphenylamine (m.); carbazole (m.); α-naphthylamine (m.); indole (w.); benzidine (w.); phenol (w.); dibenzoylmethane (v.w.); hydroquinone (v.w.); α-naphthol (m.); diphenyl ether (m.); dibenzofuran (w.); diphenylmercury (w.); phenoxthiin (w.); triphenylmethyl chloride (v.w.). These compounds all show visible "normal" phosphorescence.

Bright phosphorescence but no delayed emission was found in: acridine, 1,3-diiodonaphthalene, α-bromonaphthalene, 1,4-naphthoquinone, benzophenone.

No delayed emission was found in: azobenzene, butter yellow, carotene (α and β), benzil, luminol. These compounds also have very weak or very short-lived (<0.1 second) phosphorescence.

From these results we may conclude that almost any compound containing a lone pair of electrons, which is oxidized without too great difficulty and which has a well-marked "normal" phosphorescence, may display the delayed luminescence phenomenon. The lone pair may lie on N, O or C, as shown by the series diphenylamide, diphenyl ether, and triphenylmethide. Our crude visual estimates show that the intensity of the effect increases with the ease of oxidation of the compound and the

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[19] The relative phosphorescence and fluorescence yields of diphenylamine and carbazole derivatives will be discussed elsewhere in more detail.

[20] J. L. Magee and M. Burton, This Journal, **72**, 1965 (1950); **73**, 523 (1951).

strength of the "normal" phosphorescence. Thus, the amines give much brighter light emission than the corresponding ethers or phenols, and the metal derivatives are more brilliant than their parent acids. The most marked effects are found with the strongly phosphorescent aromatic lithium amides, which, in dry form, are instantly destroyed when exposed to air.

The nature of the solvent has a marked effect on the intensity of delayed luminescence. Thus, carbazole gives a much more intense luminescence in EPT than in EPA, and in the latter solvent, diphenyl ether and hydroquinone show no delayed luminescence at all. In this and similar cases, the amine solvent may afford better electron traps and thus enhance the luminescence. If the solvent is very basic negative ions may be formed (naphtholate, phenolate) which are more readily oxidized than the uncharged molecule. In addition, the neutral radical resulting from photoöxidation of a negative ion exerts no long range coulomb attraction on the electron, and thus even shallow solvent traps suffice to prevent immediate recombination.

In radiation chemistry the formation of triplet states by ion–electron or radical–electron recombination frequently has been assumed. Such processes, which are undoubtedly widespread, may be directly observed in these luminescent systems. Attempts have been made to identify ions and especially solvated electrons produced by X-irradiation of rigid amine solvents like EPT.[21] The results so far have been negative, possibly because the available traps were insufficiently deep to hold the electron against coulombic restoring forces. Similar negative results were obtained by Roberts and Allen[22] who looked for solvated electrons in irradiated liquid ammonia.

[21] These experiments were carried out by Dr. H. Rubin.

[22] R. Roberts and A. O. Allen, THIS JOURNAL, **75**, 1256 (1953).

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Symmetrical Semiquinone Formation by Reversible Photoöxidation and Photoreduction[1]

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In rigid solvents the illumination of *either* diphenyl-*p*-phenylenediamine *or* the corresponding imine yields a new substance having a characteristic absorption band at 7100 Å. It is shown that this compound is the semiquinone of the imine–amine oxidation–reduction couple. Thus, both photoöxidation and the inverse process of photo-reduction may occur, leading to the same semiquinone. Similar behavior is demonstrated for the hydroquinone–benzoquinone couple.

We have previously described experiments in which were demonstrated the formation of radicals and solvated electrons by illumination of readily oxidized organic molecules in rigid solvents.[2] This process of direct photoöxidation may be used to prepare a wide variety of semiquinones, as has been shown by Lewis and his school.[3,4] The radical or radical–ion remaining after electron ejection may then undergo a proton-transfer reaction on standing, to yield the ionic form of the semiquinone which is most stable in the given solvent.

In this paper, again using the rigid solvent technique to stabilize high energy intermediates, we show that the inverse process of *photo-reduction* also occurs under suitable conditions, and that the same semiquinone may be prepared by irradiating *either* the fully oxidized or fully reduced form of a given oxidation–reduction couple. For example, the irradiation in rigid solvents of either diphenyl-*p*-phenylene diamine or the corresponding imine produces a characteristic blue color. This same blue compound is obtained by chemical oxidation of the amine or reduction of the imine and its mode of preparation, oxidation–reduction titration and paramagnetism establish that it is the semiquinone (probably the doubly protonated form, RH_2^+) of the imine–amine couple.

The oxidation–reduction system hydroquinone–benzoquinone also yields the same spectrum when either the reduced or oxidized form is irradiated in rigid solution, in complete analogy with the behavior of the imine–amine couple. The new spectrum is therefore attributed to the semiquinone of hydroquinone.

Just as in reversible photoöxidation, softening of the photoreduced solution by warming restores the original spectrum.

Experimental

1. **Spectra.**—Absorption spectra at room temperature were taken with a Beckman Model DU quartz spectrophotometer. For low temperature work, a specially modified Beckman was used. The cell compartment of this instrument was replaced by a larger box and frame, holding an unsilvered Dewar. This was either a large Pyrex vessel, made from tubing selected for good optical quality or a smaller quartz flask, carrying four plane windows. Cylindrical dural-block thermostats, with dural extension rods dipping into liquid nitrogen and resting on the bottom of the flasks, were made to fit the dewars. The thermostat blocks carried vertical slots for holding the absorption cells and horizontal holes to permit passage of the light beam. Sectors were also cut out for addition of liquid nitrogen. By rotation of a vertical axial shaft, fixed to the thermostat block, either cell could be brought into the light beam. Adjustable pins, mounted on the shaft and striking a stop fixed to the frame, enabled the cells to be oriented precisely and reproducibly. Lateral motion of the cells was minimized by fitting the thermostat closely within the dewar

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[2] H. Linschitz, M. G. Berry and D. Schweitzer, THIS JOURNAL, **76**, 5833 (1954).

[3] G. N. Lewis and D. Lipkin, *ibid.*, **64**, 2801 (1942).

[4] G. N. Lewis and J. Bigeleisen, *ibid.*, **65**, 520, 2419, 2424 (1943).