position S_3S^{2-}. For any other values of $[SH^-][OH^-]$ and any other temperature, $\bar{n}$ is different from 3 and the formation of S_2^- ions is described by eq 5. In the present study no attempt was made to estimate values of K_n and thence the actual concentrations of the various polysulfides. Therefore, the experimental values of K'_d for reaction 2 obtained by assuming the absorption at 25.0 kK to be due to the sole presence of tetrasulfide ions may differ considerably from the theoretical values K_d. In order to obtain some estimate of the influence of $[OH^-]$, experimental values at 160° for K'_d at pH 6.2, 6.5, 6.8, and 7.1 are shown in Figure 3. It is obvious that the effect of $[OH^-]$ on K'_d is significant but small compared with that of temperature. The uncorrected values of K'_d, therefore, can be used to describe the formation of S_2^- ions in solutions of polysulfides containing an excess of sulfide sulfur in a simplified way by neglecting any changes in $\bar{n}$ due to variations in pH and temperature. In Figure 3 a series of values of K'_d is plotted against $1/T$. These values were obtained from solutions varying in pH from 4.7 to 10.6 and in total sulfide from 0.02 to 0.2 M. The standard deviation of pK'_d with respect to values as represented by a line fitted by the method of least squares is ±0.14. This also shows that the ratio K'_d/K_d is close to unity at all temperatures and SH^- and OH^- concentrations investigated. The thermodynamic data calculated from the temperature dependence of pK'_d as given by

$$pK'_d = -\frac{4533}{T} + 6.42 \tag{8}$$

are $\Delta H'_d = 20.7 \pm 1.2$ kcal/mol and $\Delta S'_d = 29 \pm 4$ cal/deg mol.

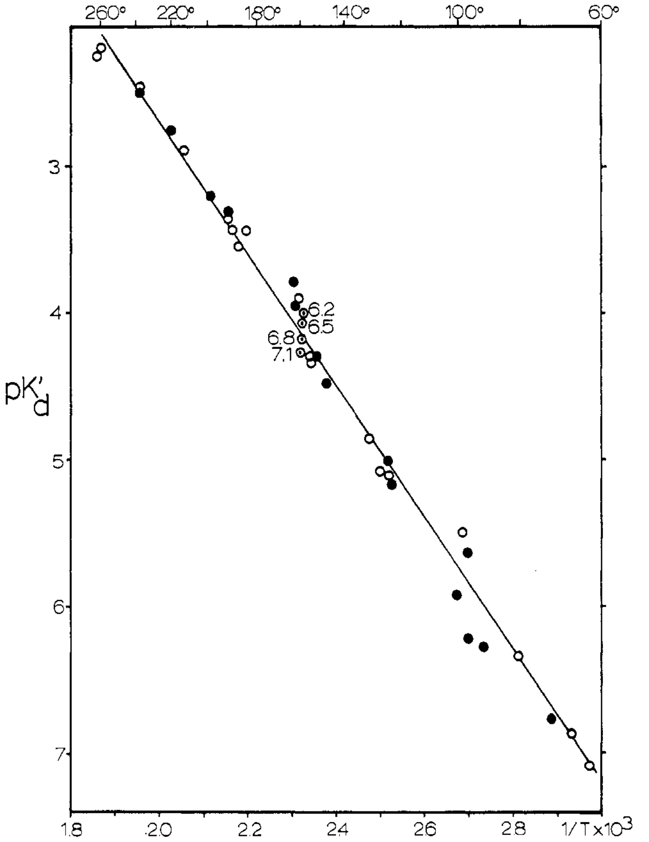

Figure 3.—Values of pK'_d as a function of $1/T$. For four points at 160° the pH of the solution is given. Open circles represent values obtained from 0.2 M and filled circles those from 0.02 M HS^-–H_2S buffer solutions.

The $\bar{n}$ values determined in this work for 160° are in agreement with the trends indicated by the data given by Teder[6] for 25 and 80°. They show that values for $\bar{n}$ exceed 4 only in solutions very low in $[OH^-]$ and $[SH^-]$ and high in S(0). With m, the number of sulfur atoms in the radical S_m^- produced by the homolytic dissociation of a polysulfide ion, eq 7, written in the more general form $2\bar{n}\sigma = 2m - 1$, indicates that with the values of σ found in this investigation the value of m is unlikely to exceed 3. Thus the possibility of the species S_8^- being formed from polysulfides existing in aqueous solution at elevated temperatures can be excluded. There was no indication of the formation of two other possible particles S_3^- and S_4^-.

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The Blue Solutions of Sulfur in Salt Melts[1]

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A deep coloration appearing in molten potassium thiocyanate above 300° was first described by Nöllner[2] in 1856 and later on by Paternò and Mazzuchelli.[3] Greenberg, *et al.*,[4] and Lux and Anslinger[5] measured the absorption spectra of these melts. Blue solutions of sulfur in alkali halide melts at temperatures above 400° were investigated by Delarue[6] and Molina,[7] whereas the preparation of a "boro-ultramarine" was reported by Hoffmann.[8] In all these cases the blue color is attributed to the formation of uncharged sulfur particles such as S_2, S_4, or colloidal sulfur. Recent spectroscopic and chemical evidence, however, suggests that these blue solutions are caused by the hypersulfide ion, S_2^-, as in organic polysulfide solutions[9] at room temperature and aqueous polysulfide solutions[10] at elevated temperatures.

Experimental Section

Materials.—All the salts used to prepare the melts were reagent grade. KSCN was dried at 120° and kept in a desiccator over P_2O_5; the LiCl-KCl eutectic was prepared and purified as described by Laitinen, et al.[11]

Borate glasses were prepared by melting weighed amounts of an equimolar mixture of K_2CO_3 and Li_2CO_3 containing 0.1% w/w of elemental sulfur in an unglazed porcelain crucible at 700°. To this clear, red-brown carbonate melt increasing amounts of B_2O_3 were added until the desired composition was reached. To

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[1] Part of this work has been carried out at the Technische Hochschule München.

[2] C. Nöllner, *Pogg. Ann.*, **98**, 189 (1856).

[3] E. Paternò and A. Mazzuchelli, *Gazz. Chim. Ital.*, **38**, 137 (1908).

[4] J. Greenberg, B. R. Sundheim, and M. Gruen, *J. Chem. Phys.*, **29**, 461 (1958).

[5] H. Lux and H. Anslinger, *Chem. Ber.*, **94**, 1161 (1961).

[6] G. Delarue, *Bull. Soc. Chim. Fr.*, 1654 (1960).

[7] R. Molina, *ibid.*, 1001 (1961).

[8] J. Hoffmann, *Z. Anorg. Allg. Chem.*, **138**, 37 (1929).

[9] W. Giggenbach, *J. Inorg. Nucl. Chem.*, **30**, 3189 (1968).

[10] W. Giggenbach, *Inorg. Chem.* **10**, 1306 (1971).

[11] H. A. Laitinen, W. S. Ferguson, and R. A. Osteryoung, *J. Electrochem. Soc.*, **104**, 517 (1957).

obtain glass disks suitable for optical investigations at room temperature, the melt was poured into 1.5-cm diameter holes in a prewarmed graphite block. The phosphate glasses were prepared in a similar way by adding potassium metaphosphate to the sulfur-containing lithium potassium carbonate melt.

The sulfide concentrations in KSCN melts were determined nephelometrically as PbS after the melts had been kept at the desired temperature for 15 min, quenched in cold water, and dissolved in distilled water.

Spectra.—Absorption spectra were determined by use of a Zeiss PM QII spectrophotometer with the monochromator M4 QIII and an attachment as described by Lux and Niedermaier.[12] This method allows the spectroscopic investigation of aggressive salt melts at elevated temperatures in a container made from some suitable material. In the present work a crucible made from pure rhodium was used. Rhodium had previously been found to withstand highly alkaline sulfide melts.[5] The thickness of the absorbing layer was 0.6 cm.

Fluorescence and excitation spectra were measured by use of the fluorescence attachment ZFM 4. X-Band esr spectra of the sulfur-doped borate and phosphate glasses were obtained with a Varian V-4500-10A spectrometer with 100-kHz modulation.

Results and Discussion

One of the oldest known phenomena appertaining to the "blue solutions of sulfur" is the deep blue coloration[2] developing in molten alkali thiocyanates at temperatures above 300°. Figure 1 shows spectra of KSCN as a function of temperature. Two bands at 17 and 25 kK can be distinguished; the strong absorption starting at 30 kK is due to the SCN^- ion. At temperatures below 300° the absorption at 25 kK is predominant, causing a slight yellow discoloration of the melt; with rising temperature, however, the strong band at 17 kK increases at a higher rate and the melt appears deep blue at 400°. After cooling the melt from this temperature to 200° the absorption at 25 kK never disappears again completely so that KSCN once heated to above 400° retains a yellowish color even at room temperature. As in the blue aqueous[10] and organic[9] solutions the absorption around 17 kK is ascribed to the S_2^-, whereas the band at 25 kK is assumed to be due largely to the presence of some polysulfide.

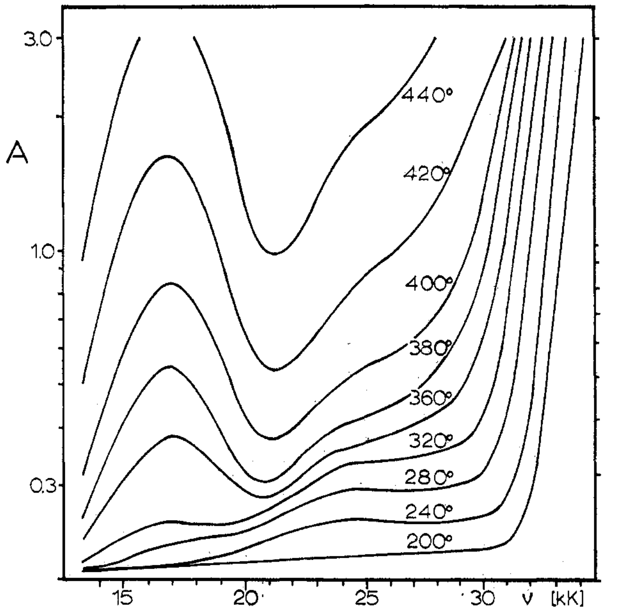

Figure 1.—Uncorrected spectra of molten KSCN as a function of temperature (d = 0.6 cm).

As indicated by the appearance of the absorption at 25 kK at temperatures below 300° the formation of S_2^- ions is preceded by the formation of polysulfide which in turn means that at lower temperatures KSCN decomposes to form sulfide according to the equation

$$2KSCN \longrightarrow K_2S + (CN)_2\uparrow$$

The dicyan produced could be detected qualitatively by the reaction with copper–benzidine paper in the atmosphere above the melt. The amounts of sulfide formed in heated and subsequently quenched KSCN melts are shown in Figure 2 together with the amount of S_2^- ions as calculated from the absorption spectra by assuming the molar absorptivity of the S_2^- ion to remain 2400 as determined in organic solutions. The strong increase in the absorption at 17 kK which appears after the addition of elemental sulfur to a melt at 250° shows that the amount of sulfide present at this temperature is sufficient to produce appreciable amounts of S_2^- ions. The reaction leading to the production of zerovalent sulfur according to the reaction $KSCN \rightleftarrows KCN + S$ thus requires a temperature above 300°.

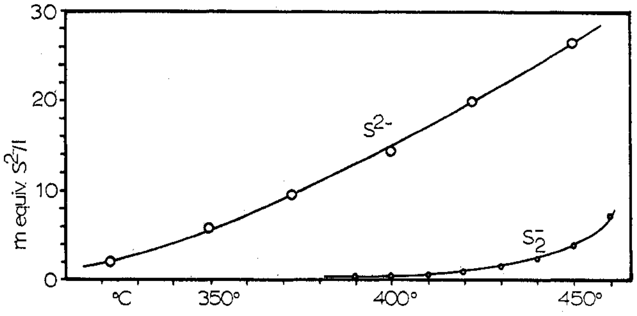

Figure 2.—Milliequivalents of sulfide present in potassium thiocyanate of elevated temperature in the form of S^{2-} and S_2^-.

Previous experiments[5] showed that the addition of 0.2% of KCN or K_2S to a KSCN melt delays the formation of the S_2^- ion by their reaction with elemental sulfur to form KSCN and K_2S_2, whereas addition of K_2S_4 causes a deep blue coloration of the melt already at 250°. This indicates that only high polysulfides are capable of dissociating into S_2^- ions, whereas S_2^{2-} appears to be stable. Therefore, the reactions occurring in a pure KSCN melt with increasing temperature may be described by the reactions

$$2KSCN \xrightarrow{>250^\circ} K_2S + (CN)_2$$

$$K_2S + KSCN \xrightarrow{>300^\circ} KCN + K_2S_2 \text{ (yellow)}$$

$$K_2S_2 + 2KSCN \overset{350^\circ}{\rightleftarrows} K_2S_4 + 2KCN$$

$$K_2S_4 \rightleftarrows 2K^+ + 2S_2^- \text{ (blue)}$$

Similar blue solutions are obtained by the addition of sulfur to molten alkali chlorides, bromides, or sulfates at temperatures above 400°. Because of their low melting point, solutions of sulfur in the LiCl–KCl eutectic were investigated in more detail. Previously the color was

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[12] H. Lux and T. Niedermaier, *Z. Anorg. Allg. Chem.*, **285**, 246 (1956).

ascribed to the presence of some polymeric form of zerovalent sulfur;[7] the strong dependence of the coloration on the "acidity" of the melt, however, favors the assumption of the formation of an ionic species. This view is strongly supported by a recent spectrophotometric study[13] of electrogenerated sulfur–sulfide solutions in fused LiCl–KCl, which lead to the conclusion that the band at 17 kK cannot be due to either sulfur or sulfide alone; the molar absorptivity of the blue species calculated for S^{2-} was found to be 4600, or 2300 calculated for S_2^-. This value is very close to $\epsilon_{\text{S}_2^-}$ 2400 used in this study.

Although it was impossible to obtain a blue coloration by the addition of sulfur to a highly purified LiCl–KCl eutectic, in the presence of traces of water vapor or hydroxides in the melt sulfur easily dissolved with deep blue color. On acidifying the melt through the addition of NaPO_3, $\text{K}_2\text{S}_2\text{O}_7$, or NH_4Cl the blue color disappears and a yellowish suspension of sulfur is formed. On the other hand, on addition of K_2CO_3 or KOH the color of the melt changed from blue to yellow or orange and the typical polysulfide spectrum with bands at 25 and 32 kK was observed. The reactions taking place in the salt melts may be described by the equations

$$n\text{S} + n\text{O}^{2-} \rightleftharpoons \text{SO}_n^{2-} + (n - 1)\text{S}^{2-} \quad (n = 3 \text{ or } 4)$$

$$3\text{S} + \text{S}^{2-} \rightleftharpoons 2\text{S}_2^- \rightleftharpoons \text{S}_4^{2-}$$

The first equation explains the dependence of the S_2^- concentration on $p\text{O}^{2-}$ in the melt. At high $p\text{O}^{2-}$, in acidic solutions, sulfide ions and therefore polysulfide and hypersulfide ions become unstable and sulfur is precipitated, whereas at low $p\text{O}^{2-}$ the large amounts of sulfide ions formed combine with zerovalent sulfur to form stable S_2^{2-} ions. The second equation describes the decrease of the absorption at 17 kK and 450° with time due to the slow evaporation of sulfur in equilibrium with sulfide and hypersulfide ions, whereas the rapid decoloration of the blue melt on cooling to temperatures below 400° can be ascribed to the dimerization of S_2^- ions to form S_4^{2-} ions, as indicated by the yellowish color of the frozen melt.

In contrast to the low-melting systems described above, with high-melting borate and phosphate melts the blue coloration and thus the S_2^- ion can be preserved at room temperature. It was found in general that melts solidifying above 600° are capable of trapping the S_2^- ion and preventing it from dimerizing to S_4^{2-}. In Table I the properties and in Figure 3 the spectra of a series of sulfur-doped borate glasses of varying acidity are given. In metaborate melts sulfur dissolves to form polysulfide ions as indicated by the absorption band at 25 kK. With increasing acidity the color of the glasses changes from red-brown through gray to blue as the absorption of the polysulfide ion diminishes and that of the S_2^- ion increases, reaching a maximum between the pentaborate and the hexaborate. This color change is accompanied by the appearance of an orange fluorescence and a three-line esr absorption in the glasses of intermediate acidity at room temperature. With the acidity exceeding that of the heptaborate, the blue color together with the fluorescence and the esr signal disappears.

Table I

Properties of a Series of Sulfur-Doped Borate Glasses Prepared from an Equimolar Mixture of Potassium Lithium Carbonate and Boron Trioxide

	Amt, g KLiCO$_3$	Amt, g B$_2$O$_3$	Color at 20°	Fluorescence at 20°	Three-line esr absorption
a metaborate	6.0	4.0	Red-brown	None	None
b tetraborate	6.0	8.0	Brown	None	Weak
c pentaborate	6.0	10.0	Gray	Orange	Strong
d	6.0	11.0	Gray-blue	Orange	Strong
e hexaborate	6.0	12.0	Blue	Orange	Strong
f heptaborate	6.0	14.0	Pale blue	Pale orange	Weak
g octaborate	6.0	16.0	Colorless	None	None

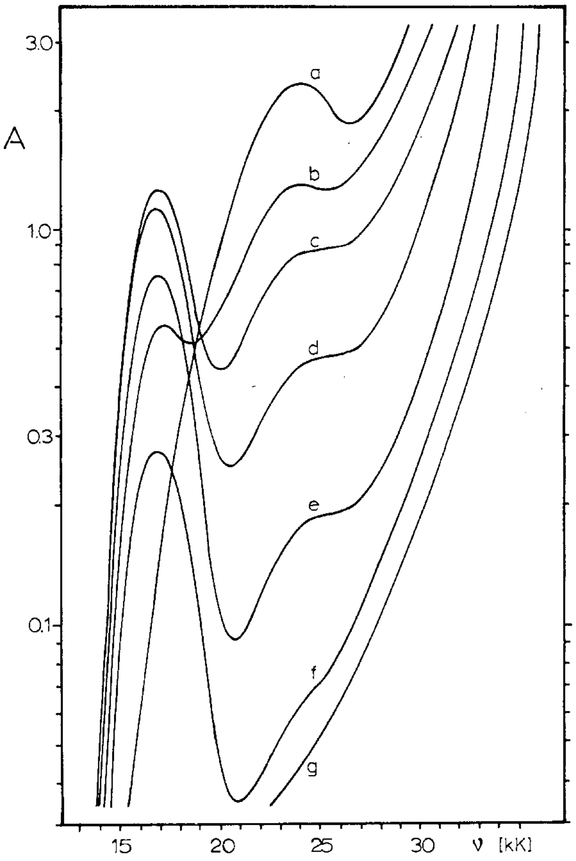

Figure 3.—Spectra of a series of borate glasses as described in Table I (d = 0.6 cm).

Similar changes in the absorption, emission, and esr spectra are observed in phosphate glasses by gradually varying the acidity from that of the potassium lithium pyrophosphate to that of the metaphosphate, with a maximum of the absorption at 17 kK and 800° in an equimolar melt of pyrophosphate and metaphosphate. The low melting point of this mixture of about 560° leads to partial dimerization of the S_2^- ion at lower temperatures and the color of the glasses at room temperature varies from green to yellow, depending on the speed of cooling. The sensitivity of the S_2^-–S_2^{2-} system toward changes in alkalinity thus offers the possibility of its use as a $p\text{O}^{2-}$ indicator for near-neutral or slightly alkaline melts.

The spectra of blue borate glasses were measured at temperatures up to 950°. The position of the band at

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(13) F. G. Bodewig and J. A. Plambeck, *J. Electrochem. Soc.*, **117**, 904 (1970).

17 kK remains essentially unchanged at all temperatures investigated. The molar absorptivity, however, decreases to about 20% of its value at room temperature. This reversible variation in the strength of the absorption is readily observed during the preparation of the glasses as they reach their deepest coloration only after complete cooling. At present no explanation for this change in intensity can be given. A similar effect is observed in the emission spectra which were measured between 20 and 300°. In this case, however, a strong shift toward higher energies from 17 to 18.5 kK is observed leading to a change in the color of the fluorescent emission from orange to greenish yellow at 300°. Together with the excitation spectrum at 23.5 kK at 20°, the observed transitions may be explained in the following simplified way. The absorption at 17 kK is due to the allowed transition from the $^2\Pi_g$ ground state of the S_2^- ion to its first excited state $^2\Pi_u$. The weak band in the S_2^- spectrum at around 24 kK, as observed in organic solution and as the excitation band in the borate glasses, then is attributed to a parity-forbidden transition from $^2\Pi_g$ to some unspecified state ^2X_g. From this state the excited molecule may return to $^2\Pi_g$ *via* a radiationless transition to $^2\Pi_u$. The remainder of the energy then is emitted during the transition from $^2\Pi_u$ to the ground state. Similar emission and excitation spectra have been reported[14] for sulfur-doped alkali halide crystals containing the S_2^- ion, thus proving the presence of this ion in sulfur-doped borate glasses and in ultramarine which also exhibits an orange emission with a maximum at 17.2 kK on exposure to long-wavelength uv radiation.

Whereas the spectroscopic data presented thus far are in agreement with the assumption of the sole formation of the S_2^- ion in polysulfide-containing melts at elevated temperatures, esr spectra indicate the presence of another radical species in significant amounts. As outlined in a previous study,[9] the S_2^- cannot be expected to exhibit any sharp detectable esr absorption except for very low temperatures. The relatively sharp three-line esr absorption with $g_1 = 2.050$, $g_2 = 2.031$, and $g_3 = 2.003$ at 90°K readily observed in blue sulfur-doped borate glasses,[15] therefore, is tentatively ascribed to the S_3^- ion. The presence of this ion was unumbiguously established in sulfur-doped alkali halide crystals;[16] it exhibited an esr absorption with $g_x = 2.049$, $g_y = 2.035$, and $g_z = 2.001$. The presence of S_3^- in addition to the S_2^- ion in ultramarine is indicated by the appearance[17] of an ir absorption at 580 cm^{-1} and the characteristic three-line esr absorption in "dilute" ultramarine.[18,19] By comparison with a DPPH standard[9] the absolute concentration of S_3^- ions in sulfur-doped borate glasses was found to vary between 10 and 15% of that of the S_2^- ion as determined by its absorbance at 17 kK. No indication of its presence, however, could be detected in the absorption spectra of borate glasses exhibiting a strong esr absorption.

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Cyclic Peroxo Complexes of Platinum(II) with α-Diketones. A Novel Preparation of "Mixed" Carboxylates

By P. J. Hayward, Sylvia J. Saftich, and C. J. Nyman*

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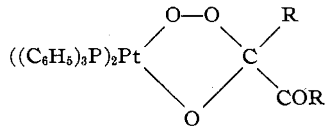
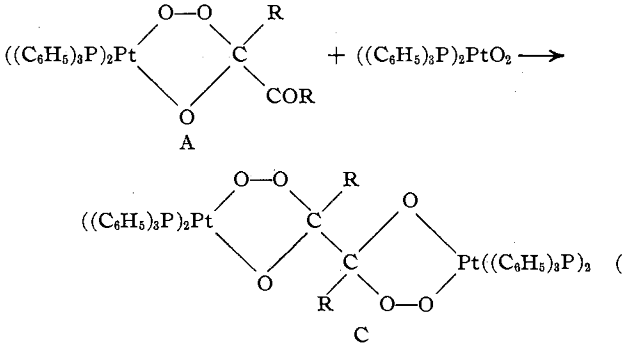
We have previously shown[1-3] that peroxobis(triphenylphosphine)platinum(II) will react with compounds containing a single carbonyl group to give adducts in which the metal and the peroxo group form part of a five-membered ring. We now report that a similar reaction will take place with α-diketones to give a product in which just one of the carbonyl groups is incorporated into the cyclic part of the structure, the other remaining "free." The initial adducts will then react with 1 further mol of $((C_6H_5)_3P)_2PtO_2$ to give a dinuclear species in which both carbonyl groups are coordinated

RCOCOR + $((C_6H_5)_3P)_2PtO_2 \longrightarrow$

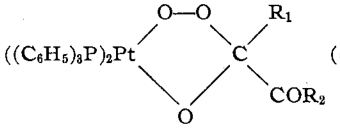


(1)



(2)

Adducts have been prepared with 2,3-butanedione ($CH_3COCOCH_3$), 2,3-pentanedione ($C_2H_5COCOCH_3$), 1-phenyl-1,2-propanedione ($C_6H_5COCOCH_3$), *p*-methoxy-1-phenyl-1,2-propanedione ($CH_3OC_6H_4COCOCH_3$), and benzil ($C_6H_5COCOC_6H_5$). With glyoxal, only a diformate could be isolated (see later). The initial products are all pale green and show the expected carbonyl stretching band due to the uncomplexed C=O at about 1700 cm^{-1} in the ir spectrum. When an unsymmetrical diketone is used, there is the possibility of forming two isomers of the initial adduct



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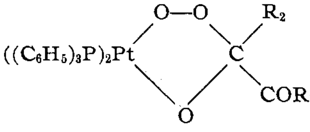

B

and, in general, a mixture was obtained. We have

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[3] P. J. Hayward and C. J. Nyman, *ibid.*, **93**, 617 (1971).