The Effect of Pressure on the Electronic Absorption Spectra of Alkali Metal Cation-Chloranil and -Bromanil Anion Radical Salts, and the Dimerization of the Chloranil Anion Radical in Solution

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The pressure dependence, up to 7 kbar, of the electronic absorption spectra of ion-radical salts composed of the alkali metal cation and the chloranil or bromanil anion radical in the crystalline state at room temperature, and the temperature dependence, down to 134°K, of the dimerization of chloranil anions in an ethanol solution at 1 bar have been studied. The absorption band in the visible region shows a blue shift with an increase in the pressure for Li^+ and Na^+ salts, while for K^+ and Rb^+ salts the spectra are insensitive to the pressure. The anion radicals seem to be in the dimeric electronic state for the former and to be in the monomeric state for the latter, in the crystalline state.

The magnetic and electronic properties of the ion-radical salts, such as Würster's blue perchlorate (WBP) and tetracyanoquinodimethane (TCNQ) salts, have attracted interest in connection with the behavior of the unpaired electrons and the characteristic intermolecular interactions in the crystalline state, and their properties under high pressure have been studied in order to get useful information on the electronic structure of ion-radical salts in the crystalline state.[1-6]

The electronic absorption spectra of ion-radical salts have been studied extensively in solution and solid states since Hausser and Murrell[7] pointed out that the new lowest-energy absorption band of the dimer in WBP, which exists in solution at low temperatures, is the charge-transfer band between the half occupied orbitals of component radicals. For example, in the case of Würster's salts, the electronic structures in the crystalline state have been discussed on the basis of the following data; the polarized reflectance spectra of WBP at temperatures above and below the phase transition point,[8] the polarized absorption spectra of some Würster's salts at room temperature,[9,10] and a comparison between the temperature dependence of the charge-transfer band intensity and that of the magnetic susceptibility.[11] On the other hand, Pott and Kommandeur[12] suggested a disproportionation of charges in a crystal which differed from dimerization.

In this paper, the effect of pressure on the electronic absorption spectra of ion-radical salts composed of an alkali metal cation and a chloranil or bromanil anion radical ($M^+(CA)^-$, M:Li, Na, K, and Rb, CA:chloranil, $M^+(BA)^-$, M:Na and K, BA: bromanil) will be investigated in order to determine the influence of the counter ions upon the electronic structures of chloranil or bromanil anion radicals in the crystalline state; also, the dimerization of chloranil anions in an ethanol solution at low temperatures and at 1 bar will be reported.

Experimental

Commercially-available *p*-chloranil and *p*-bromanil synthesized by the method of Torrey and Hunter[13] were purified by recrystallization from benzene and then by sublimation *in vacuo*. Their alkali metal salts were synthesized according to the method of Torrey and Hunter;[13] lithium and rubidium salts were synthesized by a method similar to that used for potassium salt. The ethanol was purified by distillation.

The optical measurements were carried out with a Cary recording spectrophotometer, Model 14M, or with a Shimadzu SV-50A spectrophotometer. The electronic absorption spectra of crystalline powder were measured on samples rubbed on glass plates, because the methods using the KBr disk and liquid paraffin mull, which are usually used for powder samples, were unsuitable for the measurements of the electronic absorption spectra of some ion radical salts because of the influence of the applied force at the time of the disk formation upon their electronic states, and for the measurements of the pressure dependence on the spectra, respectively. The spectra at low temperature were measured by using a Pyrex Dewar vessel and using liquid nitrogen as a refrigerant, the temperature being measured by means of a copper-constantan thermocouple. The spectra under high pressure at room temperature were measured by using a high-pressure optical cell which had two sapphire windows. A hydrostatic pressure up to 7 kbar was applied by means of a pressure-transmitting medium, white gasoline, through a pressure-intensifier. The pressure was determined by a Harwood manganine resistance gauge and a Heise Bourdon tube gauge.

Results and Discussion

A. Absorption Spectra in the Crystalline State. The electronic absorption spectra of four alkali metal cation-chloranil anion-radical salts measured on crystalline

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[1] A. W. Merkl, R. C. Hughes, L. J. Berliner, and H. M. McConnell, *J. Chem. Phys.*, **43**, 953 (1965).

[2] R. C. Hughes, A. W. Merkl, and H. M. McConnell, *ibid.*, **44**, 1720 (1966).

[3] R. B. Aust, G. A. Samara, and H. G. Drickamer, *ibid.*, **41**, 2003 (1964).

[4] I. Shirotani, T. Kajiwara, H. Inokuchi, and S. Akimoto, This Bulletin, **42**, 366 (1969).

[5] I. Shirotani, N. Sakai, H. Inokuchi, and S. Minomura, *ibid.*, **42**, 2087 (1969).

[6] N. Sakai, I. Shirotani, and S. Minomura, *ibid.*, **43**, 57 (1970).

[7] K. H. Hausser and J. N. Murrell, *J. Chem. Phys.*, **27**, 500 (1957).

[8] G. R. Anderson, *ibid.*, **47**, 3853 (1967).

[9] Y. Iida and Y. Matsunaga, This Bulletin, **41**, 2615 (1968).

[10] J. Tanaka and M. Mizuno, *ibid.*, **42**, 1841 (1969).

[11] T. Sakata and S. Nagakura, *ibid.*, **42**, 1497 (1969).

[12] G. T. Pott and J. Kommandeur, *J. Chem. Phys.*, **47**, 395 (1967).

[13] H. A. Torrey and W. H. Hunter, *J. Amer. Chem. Soc.*, **34**, 702 (1912).

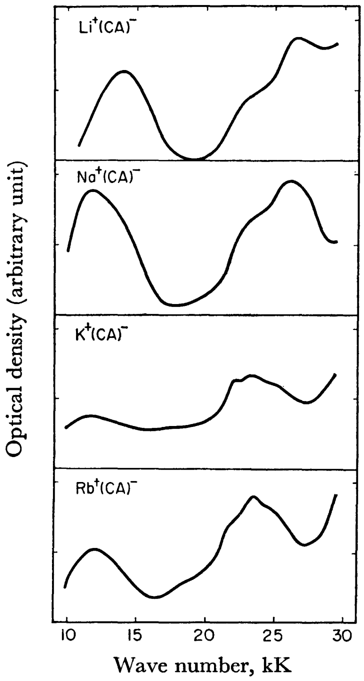

Fig. 1. Electronic absorption spectra of four alkali metal cation-chloranil anion radical salts.

powder samples rubbed on glass plates are shown in Fig. 1.[14] The spectra of Na$^+$(CA)$^-$ and K$^+$(CA)$^-$ almost coincide with the recent work of André and Weill.[15] The absorption spectra of Li$^+$(CA)$^-$ and Na$^+$(CA)$^-$ show considerable differences from those of K$^+$(CA)$^-$ and Rb$^+$(CA)$^-$: that is, in the visible region, the former shows the absorption band around 26 kK, with a shoulder around 23 kK, while the latter shows the band with structures around 22.0, 23.3, and 24.5 kK, and the ratio of the absorption-band intensity in the near-infrared region to that in the visible region is larger for the former than for the latter.[16] The absorption band in the near-infrared region of Li$^+$(CA)$^-$ is around 14 kK; this energy is 2 kK higher than those of the other salts.

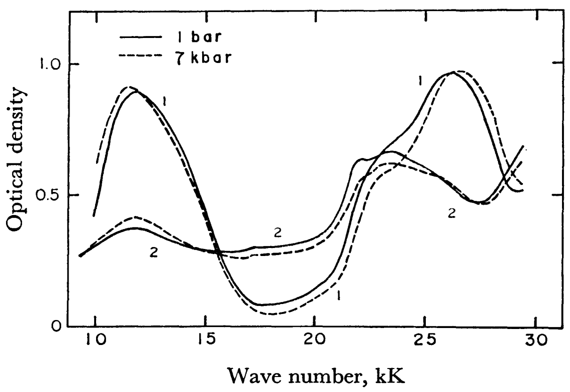

Fig. 2. Pressure dependence of the absorption spectra of crystalline Na$^+$(CA)$^-$ and K$^+$(CA)$^-$, curve 1: Na$^+$(CA)$^-$, curve 2: K$^+$(CA)$^-$.

The effect of pressures up to 7 kbar on the electronic absorption spectra of these salts was measured at room temperature. The absorption spectra of Na$^+$(CA)$^-$ and K$^+$(CA)$^-$ at 1 bar and 7 kbar are shown in Fig. 2. Li$^+$(CA)$^-$ and Na$^+$(CA)$^-$ exhibit a blue shift for the visible absorption band and a red shift for the near-infrared band, with an increase in the pressure. The rates of the frequency shift with the pressure are $+62$ and -58 cm^{-1}/kbar for the 26.2 and 11.8 kK peaks of Na$^+$(CA)$^-$ respectively, as is shown in Fig. 3 and as has previously been reported briefly[5]; those of Li$^+$(CA)$^-$ are almost the same. On the other hand, in the cases of K$^+$(CA)$^-$ and Rb$^+$(CA)$^-$, the absorption spectra are insensitive to the pressure: that is, no effect of the pressure is observed, at least up to 7 kbar, except for a slight change in the band intensity of K$^+$(CA)$^-$ (Fig. 2).

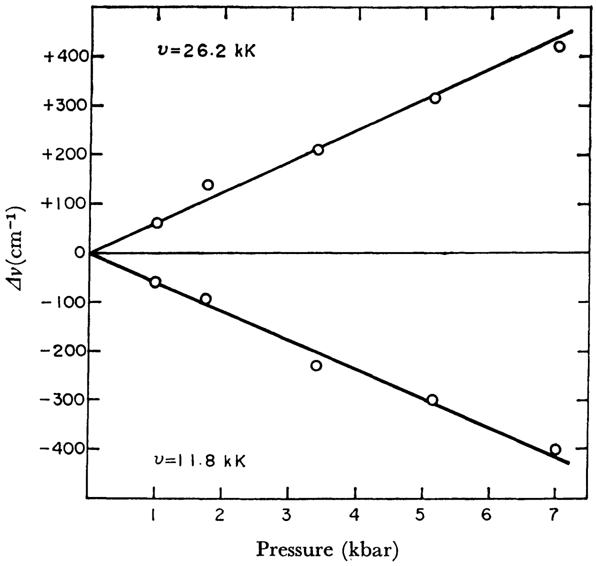

Fig. 3. Frequency shift with pressure for 26.2 and 11.8 kK peaks of Na$^+$(CA)$^-$.

These pressure effects, in particular, a large pressure-induced blue shift of the band in the visible region, suggest that chloranil anions associate bimolecularly in the crystalline state in Li$^+$(CA)$^-$ and Na$^+$(CA)$^-$. This is analogous to the situation with alkali metal cation-TCNQ anion radical salts in the crystalline state, where the absorption spectra are similar to those of the radical dimer (TCNQ$^-$)$_2$ in an aqueous solution, and where, in the visible region, there is a large blue shift with an increase in the pressure. This shift has been discussed in connection with the stabilization of the electronic-ground state from the characteristic crystalline structure (stacked face-to-face) of TCNQ anions and the crystal-field effect of the metal cations surrounding the TCNQ anions.[6] Therefore, we investigated whether or not the dimerization of the chloranil anion occurs in solutions,

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[14] As a test of the reliability of this method, the absorption spectra of single crystals of K$^+$ (CA)$^-$ in the visible region were measured by using a microspectrophotometer. The spectra measured by the present method agree well with those measured on single crystals.

[15] J. J. André and G. Weill, *C. R. Acad. Sci., Paris, Ser. B*, **269**, 499 (1969).

[16] The spectra of Rb$^+$ (CA)$^-$ obtained by the method of the KBr disk are similar to those of Na$^+$ (CA)$^-$ in the visible region; therefore, when the method of the KBr disk is used, some attention should be taken.

as has been observed in a solution of Würster's cation,[17] the *p*-benzosemiquinone anion,[18] and the TCNQ anion;[19] consequently, a monomer-dimer equilibrium for $(CA)^-$ is confirmed in an ethanol solution at low temperatures (see the next section, B).

The absorption spectra of crystalline $Li^+(CA)^-$ and $Na^+(CA)^-$ are similar to those of the dimer in solution, while the spectra of $K^+(CA)^-$ and $Rb^+(CA)^-$ are similar to those of the monomer in solution except for the weak near-infrared absorption band in the crystalline state. Although the dimerization of the chloranil anion in solution is observed in all four alkali metal cation-chloranil anion radical salts, $K^+(CA)^-$ and $Rb^+(CA)^-$ show an electronic structure with the nature of the monomer in the crystalline state.

The X-ray diffraction powder patterns of $Na^+(CA)^-$ and $K^+(CA)^-$ at room temperature, in which slight differences are observed from sample to sample, show a remarkable difference in the crystalline nature between the two salts, as is shown in Fig. 4.

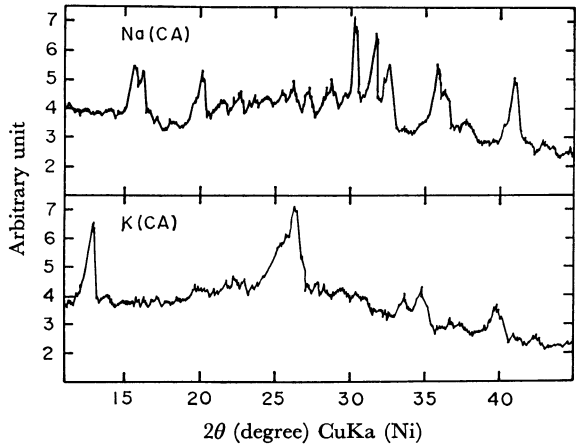

Fig. 4. X-ray diffraction powder patterns of $Na^+(CA)^-$ and $K^+(CA)^-$ at room temperature.

The ionic radii of Li^+, Na^+, K^+, and Rb^+ are 0.78, 0.98, 1.33, and 1.49 Å, respectively, where the increase from Na^+ to K^+ is marked.[20] The polarizing powers, which are equal to Ze/r^2 (Z: number of charge, e: elementary charge, r: ionic radius), are 1.64, 1.04, 0.57, and 0.45 (arbitrary unit) for Li^+, Na^+, K^+, and Rb^+ respectively, where the values for Li^+ and Na^+ are much larger than those for K^+ and Rb^+.[20] That is, Li^+ and Na^+ have a stronger power to distort the opponent electron cloud than K^+ and Rb^+, and the effect of this power cannot be ignored for a molecule with π-electrons. Although alkali metal cation-TCNQ anion radical salts show little difference in the electronic structure of TCNQ anions in the crystalline state, in the case of alkali metal cation-chloranil anion radical salts, the packing and the electronic structure of the chloranil anions in the crystalline state may be considerably affected by the size and the polarizing power of the counter ion; consequently, chloranil anions seem to be dimeric in $Li^+(CA)^-$ and $Na^+(CA)^-$, the alkali metal cations of which have small ionic radii and large polarizing powers.[21] On the other hand, chloranil anions seem to be monomeric, with a weak interaction between anion radicals in $K^+(CA)^-$ and $Rb^+(CA)^-$[21]; it also seems that their absorption spectra are insensitive to the pressure because of the weak inter-radical interaction and seem to be less compressible because of the large ionic radii.

In the case of bromanil salts, the absorption spectra of crystalline $K^+(BA)^-$ are similar to those of crystalline $K^+(CA)^-$, and the effect of pressure on the absorption spectra was not observed, at least up to 7 kbar; the absorption spectra of crystalline $Na^+(BA)^-$ are diffused and are not clear, but they seem to be characteristic of both of the monomer and the dimer of BA^-. The spectra of $Na^+(BA)^-$ obtained by the method of the KBr disk are, however, similar to those of $Na^+(CA)^-$ and behave the same as $Na^+(CA)^-$ under high pressures. The dimerization of the bromanil anion was not observed in an ethanol solution down to the temperature of liquid nitrogen. The X-ray diffraction powder patterns of $Na^+(BA)^-$ and $K^+(BA)^-$ at room temperature resemble each other.

The phase transition accompanying a change in the electronic structure, as has been observed in WBP,[8,11,12,22] should be expected to occur in these chloranil and bromanil anion radical salts in which the intermolecular interaction between anion radicals differs from radical to radical.

B. Dimerization of Chloranil Anion Radical in Ethanol.

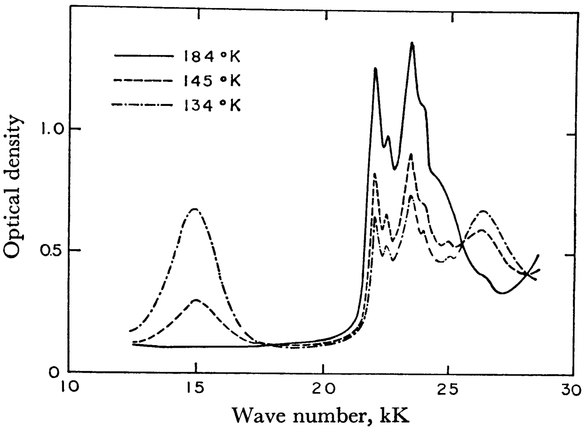

Fig. 5. Temperature dependence of the absorption spectra of $Na^+(CA)^-$ in ethanol.
Stoichiometric concentration: 3.7×10^{-4} mol/*l*. (at 293°K)
Optical path length: 0.40 cm.

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17) K. Uemura, S. Nakayama, Y. Seo, K. Suzuki, and Y. Ooshika, This Bulletin, **39**, 1348 (1966).

18) K. Kimura, H. Yamada, and H. Tsubomura, *J. Chem. Phys.*, **48**, 440 (1968).

19) R. H. Boyd and W. D. Phillips, *ibid.*, **43**, 2927 (1965).

20) V. M. Goldschmidt, "Geochemische Verteilungsgesetze der Elemente VII, Die Gesetze der Krystallochemie," Skrifter Norske Videnskap Akad. Oslo. I Mat-Naturv, Kl. (1926).

21) From the temperature dependence of the intensities of the ESR spectra, it has been observed that, in the temperature range from 290°K to 370°K, the singlet-triplet model was approximately followed, with δ=0.16 eV (the singlet-triplet energy separation) for $Na^+(CA)^-$, whereas the Curie-Weiss law was followed for $K^+(CA)^-$. These results would appear to be coincident with the electronic structure of chloranil-anion radical salts assumed from the electronic absorption spectra

22) H. Chihara, M. Nakamura, and S. Seki, This Bulletin, **38**, 1776 (1965).

When an ethanol solution of alkali metal cation-chloranil anion radical salts, a solution which is yellow at room temperature, is cooled to about 145°K, it turns green and new absorption bands appear in the electronic absorption spectra. The temperature dependence of the absorption spectra of $Na^+(CA)^-$ in ethanol is show nin Fig. 5. The absorption band around 22 kK may be attributed to the lowest energy π–π^* transition in the chloranil anion monomer.[23,24] From the concentration dependence (between 10^{-3} and 10^{-4} mol/l) of the absorption intensity of $Na^+(CA)^-$ in ethanol, the monomer and dimer of the chloranil anion radical can be said to be in equilibrium in solution. The thermodynamic quantities of dimerization are obtained by the following procedure.

An equilibrium of the degree of association of n for the anion radical is assumed:

$$n(\mathrm{CA})^- \rightleftharpoons (\mathrm{CA}^-)_n \qquad (1)$$

The equilibrium constant, K, is given by:

$$K = (1-\alpha)/(nc^{n-1}\alpha^n) \qquad (2)$$

where c is the stoichiometric concentration[25] of $Na^+(CA)^-$ and where α is the fraction of the stoichiometric concentration existing as a monomer. The apparent molar extinction coefficient at a certain wavelength is related to the molar extinction coefficients of the monomer and n-polymer as:

$$\varepsilon = \alpha\varepsilon_m + (1-\alpha)\varepsilon_n \qquad (3)$$

where ε is the apparent molar extinction coefficient, as calculated from the measured optical density and the concentration, where ε_m is the molar extinction coefficient of the monomer, and where ε_n is the molar extinction coefficient of one molecule in the n-polymer. The values of ε_m at several peaks are determined from the optical density measured at higher temperatures (190—170°K), where it seems that no association of the radicals occurred.[26] From the relation of Eqs. (2) and (3), the following equation is obtained:

$$\log\{c(1-\varepsilon/\varepsilon_m)\} = \log(\mathrm{B}K) + n\log c(\varepsilon-\varepsilon_n)/\varepsilon_m\} \qquad (4)$$

where:

$$\mathrm{B} = n(1-\varepsilon_n/\varepsilon_m)^{1-n}$$

Therefore, assuming $\varepsilon \gg \varepsilon_n$, Eq. (4) leads to:

$$\log\{c(1-\varepsilon/\varepsilon_m)\} = \log(\mathrm{B}K) + n\log(c\varepsilon/\varepsilon_m) \qquad (5)$$

When $\log\{c(1-\varepsilon/\varepsilon_m)\}$ is plotted against $\log(c\varepsilon/\varepsilon_m)$ for the monomer band (λ_{max}=427 mμ) at 134°K, the slope of the straight line, n, is about 2. This means that the concentration dependence of the absorption spectra of $Na^+(CA)^-$ in ethanol at low temperatures can be explained by the equilibrium between the monomer and the dimer. The value of ε_d[27] is chosen to give a straight line with a slope of 2 when $\log\{c(1-\varepsilon/\varepsilon_m)\}$ is plotted against $\log\{c(\varepsilon-\varepsilon_d)/\varepsilon_m\}$, as is shown in Fig. 6: using this value of ε_d, the value of K is evaluated from Eq. (4). The ε_d values at other peaks are evaluated using Eq. (3) from the measured ε, ε_m, and α values, calculated from ε, ε_m, and ε_d at 427 mμ using Eq. (3). The molar extinction coefficients at several peaks are shown in Table 1.

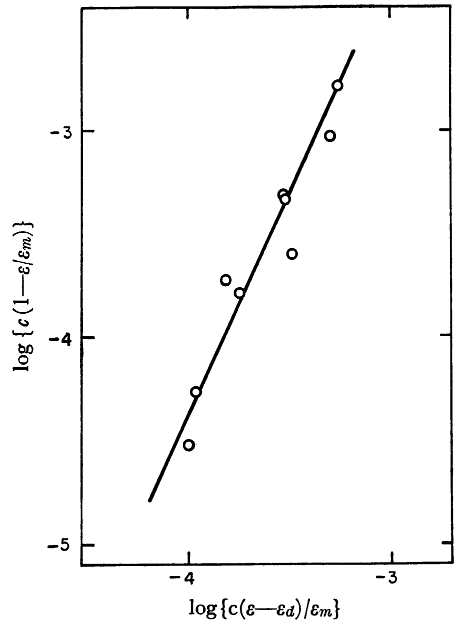

Fig. 6. Plots of $\log\{c(1-\varepsilon/\varepsilon_m)\}$ against $\log\{c(\varepsilon-\varepsilon_d)/\varepsilon_m\}$ for the monomer band (λ_{max}=427 mμ) at 134°K.

TABLE 1. MOLAR EXTINCTION COEFFICIENTS OF $Na^+(CA)^-$ IN ETHANOL

Absorption peak	ε_m	$2\varepsilon_d$
3800 Å (26.3 kK)	1700	9700
4270 (23.4 kK)	8500	1800
4545 (22.0 kK)	7700	1300
6700 (14.9 kK)	200	13600

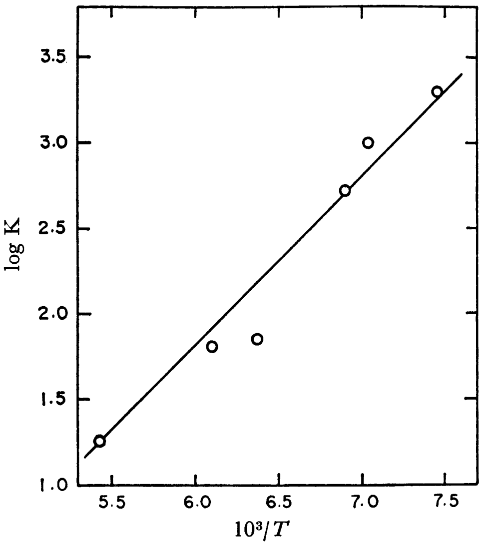

Fig. 7. Plots of log K against $10^3/T$ (°K)$^{-1}$ for the monomer band.

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[23] G. Giacometti, P. L. Nordio, and G. Rigatti, *Nuovo Cimento*, **23**, 433 (1962).

[24] J. J. André and G. Weill, *Mol. Phys.*, **15**, 97 (1968).

[25] Volume changes in solution with the temperature were taken into account.

[26] The solution is stable at low temperatures, but it is slowly discolored at room temperature.

[27] Here the ε_n in Eq. (4) is rewritten as ε_d.

Table 2. Thermodynamics of dimerization of CA$^-$ at 134°K

K (l/mol)	ΔF (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol·deg)
2.0×10^3	-2.0	-4.5	-18.7

A series of spectra at various temperatures on one solution is measured, and the equilibrium constant, K, at each temperature is calculated from α, obtained from the data at 427 mμ, using Eq. (2): in Fig. 7 log$K$ is plotted against $1/T$. The thermodynamic quantities are shown in Table 2.

The dimerization in ethanol at low temperatures is observed for Li$^+$(CA)$^-$, K$^+$(CA)$^-$, and Rb$^+$(CA)$^-$, too. The thermodynamic quantities for other salts are of interest with regard to the influence of the counter ion upon the dimerization of CA$^-$.

The dimerization of CA$^-$ is observed in an aqueous solution at room temperature, but it is very unstable in air.28)

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28) R. Foster and T. J. Thomson, *Trans. Faraday Soc.*, **59**, 296 (1963). This fact has been reported together with the absorption maxima of alkali metal salts of chloranil anion in tetrahydrofuran at —50°C.