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Photobromination of Pentane

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monium bromide, where marked hysteresis was observed. These results are in satisfactory agreement with those of Mandleberg and Staveley, although at small concentrations of ammonium bromide our temperatures are somewhat lower.

In a more recent investigation[3] of the heat capacity of pure ammonium bromide, another transition was found at about 78°K on cooling, and 108.5°K on warming. This transition corresponds to the transformation at 169°K in ND_4Br.[4]

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[1] C. J. Mandleberg and L. A. K. Staveley, J. Chem. Soc. 2736 (1950).
[2] B. Cochet-Muchy and R. A. Paris, Compt. rend. **232**, 1930 (1951).
[3] Stephenson, Cole, and Landers (to be published).
[4] Clusius, Kruis, and Schanzer, Z. anorg. u. allgem. Chem. **236**, 26 (1938).

Spectra of Material Ejected from Plaster by the Impact of Ultraspeed Pellets

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As part of the experimentation conducted to study the shapes of craters formed in plaster of paris by ultraspeed pellets,[1] several spectrograms were taken of the impact of the pellet on the plaster to observe the vaporization, if any, of the plaster material. The experimental arrangement was the same as that used for the examination of the spectra of ultraspeed pellets[2] except that a plaster block was placed adjacent to the slit and perpendicular to the face of the spectrograph. With this arrangement, pellets were fired across the slit into the plaster block.

Two types of pellets were fired; one type was made of a special magnesium-lithium-aluminum alloy and the other was of aluminum. The velocity of impact was 5.5 km/sec and 4.5 km/sec, respectively.

Along with the lines and bands of the spectrum of the ultraspeed pellet, calcium lines and calcium oxide bands were identified. These were $\lambda\lambda4227$ due to Ca; $\lambda\lambda5473$ to 5602 due to Ca and CaO; and $\lambda\lambda5983$ to 6097 and $\lambda\lambda6183$ to 6362, both due to CaO.

It is evident from the spectrograms that there is a considerable amount of vaporization of the plaster material.

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[1] J. S. Rinehart and Wm. C. White, Am. J. Phys. **20**, 14 (1952).
[2] White, Rinehart, and Allen, J. Appl. Phys. **23**, 198 (1952).

Phase Transitions of the Barium Dicalcium *n*-Butyrate

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We have reported[1] the crystal structure of cubic barium dicalcium *n*-butyrate, $BaCa_2(CO_2CH_2CH_2CH_3)_6$, in which alkyl groups within ionic radicals are rotating, and we have suggested phase transitions which might be attributed to possible changes in rotational modes. We have recently found two phase transitions on this crystal and will give a brief account of our investigation.

The observation under the polarizing microscope shows that by slow cooling the cubic modification changes into an anisotropic one at 5.2°C without remarkable shattering, and by heating it from room temperature up to about 100°C it shows no appreciable changes in appearance. By means of the usual dilatometry, we found two volume changes at about 5.2°C and 50.2°C (Fig. 1), the dilatometer liquids used being evacuated mercury, liquid paraffin, and xylene. The results of the differential thermal analysis, using pure rock salt as standard material, are illustrated in Fig. 2. The double peaks of the lower transition somewhat resemble those in the transition of barium dicalcium propionate at −6.0°C. The peak of the upper transition is very small and flat. The dielectric constant of the powdered sample at 50 kc increases a little, on heating, at 5.2°C, whereas at 50.2°C there is no detectable change.

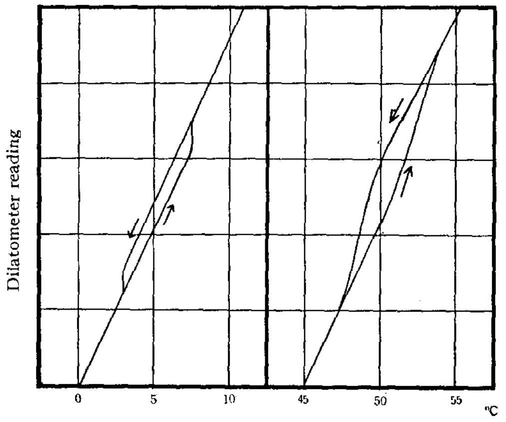

Fig. 1. The dilatometry of $BaCa_2(CO_2CH_2CH_2CH_3)_6$. The cubic thermal expansion coefficient is about 0.2 cc/1 gr mole. The volume change for the lower transition is about 0.3 and for the upper 1.0 cc/1 gr mole, respectively.

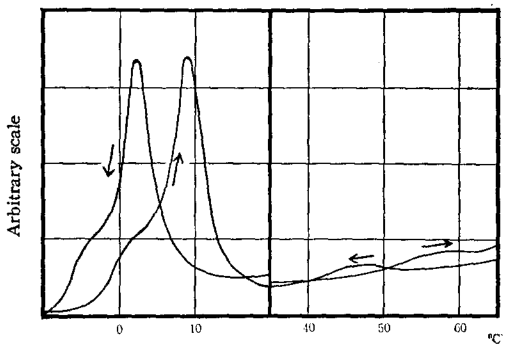

Fig. 2. Differential thermal analysis of barium dicalcium *n*-butyrate. The heating rate of the specimen is about 10 min/deg.

From these results we may deduce a tentative explanation of the mechanism of the transitions as follows: In the lowest anisotropic phase the rotational motion of the *n*-butyrate ion at room temperature is frozen and assumes a lower symmetry. The weak upper transition which is of the higher order type may be looked upon as related to the positional transfer of the carboxyl oxygen atoms between two alternatives.

We thank Professor I. Nitta, Professor T. Watanabe, and Professor S. Seki for their kind encouragement.

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[1] Oda, Sakata, and Kondo, J. Chem. Phys. **19**, 1314 (1951).
[2] Seki, Momotani, and Nakatsu, J. Chem. Phys. **19**, 1061 (1951).

Photobromination of Pentane

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It is claimed by Williams and Hamill[1] that "in the photobromination of gaseous *n*-pentane with visible light at 80°, the ratio of all the lower bromides to amyl bromide appears to be approximately 30:70." This ratio was arrived at by addition of appropriate carrier substances to the bromination mixture obtained when radioactive bromine of a high specific activity was used.

It seemed highly improbable that organic chemists had overlooked the formation of such large quantities of lower bromides, as claimed by Williams and Hamill, in the bromination of normal hydrocarbons. A study was therefore made of the products formed in the vapor phase bromination of *n*-pentane at 80°. Over 94 percent of the theoretically possible amount of bromine used was recovered as amyl bromides, with the rest probably swept out of the apparatus with the hydrogen bromide gas formed in the reaction. A very careful but unsuccessful search was made for low boiling alkyl bromides.

Therefore, it appears to us that the statement of these investigators,[1] "In conclusion, we wish to emphasize that the experimental evidence for considerable fragmentation of the carbon chain in photobromination of *n*-pentane at 80°C seems to us quite inescapable," must be regarded with considerable reserve by organic chemists, and that the technique which led to their erroneous conclusion should be critically examined.

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[1] Williams and Hamill, J. Am. Chem. Soc. **72**, 1857 (1950); Hamill, Williams, and Voiland, Brookhaven Conference Report No. 4, p. 90 (1950).

Reduction Potentials and Unsaturation Energy Changes in Electrode Reactions Leading to the Formation of Acridyl Radicals

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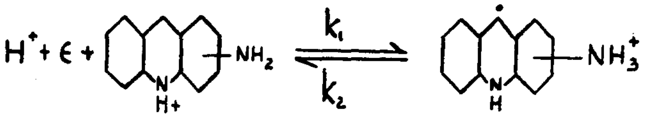
THE occurrence of stable semiquinones as intermediates in the reduction of some phenazines has been studied in detail,[1] mainly by potentiometric methods; but although it has often been proposed that semiquinone formation occurs in reactions involving the corresponding mono-aza hydrocarbons, the acridines,[2] quantitative data for these systems have only recently become available.

I II

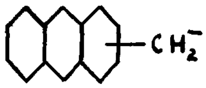
FIG. 1. Radical types considered.

The two-step reduction of a series of aminoacridines at the mercury capillary electrode has been studied by Kaye and Stonehill[3] under conditions such that specific adsorption effects (complications arising from which often obscure the significance of current-potential data for systems involving semiquinones) are absent, or are at least greatly minimized. The aminoacridines, in general, reduce in two one-electron steps, both of which may be *p*H-dependent; the first step leads to the formation of radicals of types I or II (Fig. 1), depending on the acidity of the solution.



III II

FIG. 2. Reaction of ionized aminoacridine II from radical of type II.



IV

FIG. 3. Anthracenemethyl anion, type IV.

These measurements are useful, as they constitute the only case where quantitative information on semiquinone formation is available over a range of systems of which the oxidants are conjugated molecules which are iso-π-electronic with each other. This being so, it is of interest to inquire whether there is a correlation between the observed reduction potentials and the changes in π-electron energy accompanying the electrode reaction.

In this preliminary treatment, attention is confined to the reaction in which ionized aminoacridine (III) is reduced to an ionized acridyl of type II, as in Fig. 2. Where the rates of all other reactions affecting the concentration of III and II at the electrode interface are small compared to the (composite) rates $k_1(\mathrm{III})(\mathrm{H}^+)$ and $k_2(\mathrm{II})$ at potentials in the vicinity of the half-wave point, we may write,* for a series of aminoacridines,

$$F\delta V_{\frac{1}{2}} = -\delta(\Delta G_a) \simeq \delta Q_a, \tag{1}$$

where $V_{\frac{1}{2}}$ is the half-wave potential, F is the Faraday, and ΔG_a and Q_a are, respectively, the free energy change and the exothermicity of the reaction in Fig. 2.

The conditions under which (1) is valid are not completely fulfilled for these systems; but, on the assumption that H^+ participates in the transition state of reaction, it may be assumed[4] that partial irreversibility of Fig. 2 will modify the relationship

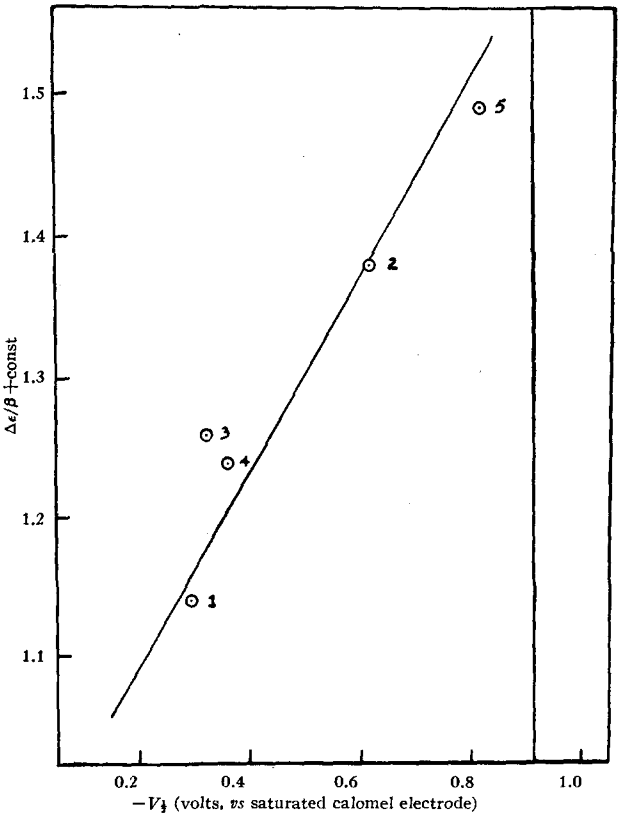


FIG. 4. Observed value of half-wave potential plotted against $\Delta\epsilon/\beta$.