



# Effect of Pile Irradiation on Sodium Chlorate

L. J. Sharman and K. J. McCallum

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average cross section of the polymer molecule in terms of fibrinogen units by comparing M/L for monomer and polymer. The results given in Table I are a striking indication that the polymerization of fibrinogen, in this instance, involves a lateral dimerization together with the longitudinal polymerization of much greater extent. Other work,<sup>6</sup> under rather different conditions, has also yielded evidence, though perhaps less directly, of the dimerization process.

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#### Effect of Pile Irradiation on Sodium Chlorate

L. J. SHARMAN AND K. J. MCCALLUM Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan, Canada (Received January 10, 1955)

THE chemical effects following the  $Cl^{37}(n,\gamma)Cl^{38}$  reaction and the  $Cl^{35}(\gamma,n)Cl^{34}$  reaction in crystalline sodium chlorate have been previously investigated.<sup>1,2</sup> The retention of chlorine activity in the form of chlorate ion was found to be small for these two reactions, about 2 percent and 9 percent respectively. The present note reports an attempt to investigate the effects following the  $Cl^{35}(n,\gamma)Cl^{36}$  reaction in the same substance.

Because of the long half-life of Cl36 it was necessary to carry out the irradiation using a high flux of thermal neutrons. Recrystallized and dried samples were irradiated in the Harwell pile for a period of 24 weeks in a position where the neutron flux was reported to be  $4 \times 10^{12}$ /cm<sup>2</sup>/sec. After irradiation, the samples were allowed to stand at room temperature for a period of six months to permit radioactive decay of short-lived activities. At the end of this time, the activity was due mainly to Cl<sup>36</sup> and S<sup>35</sup>.

The samples were analyzed chemically to identify the substances present. The percentages of sodium chloride, sodium chlorate, and sodium perchlorate are shown in Table I. Less than 0.1 percent of

TABLE I.

Fraction	Weight percent composition	Molar ratio	Percent Cl <sup>36</sup> activity	Ratio of Cl <sup>36</sup> activity/mole
NaCl	14.50±0.03	0.33	86.5±3.0	21 ±1
NaClO <sub>3</sub>	81.8 ±0.2	1.00	$12.7 \pm 0.3$	1.0
NaClO <sub>4</sub>	$3.8 \pm 0.2$	0.04	$0.5 \pm 0.05$	$1.1 \pm 0.14$

the chlorine was present in compounds with intermediate valence states, such as chlorine, chlorine dioxide, chlorite, or hypochlorite.

The distribution of the Cl<sup>36</sup> activity between the chloride, chlorate, and perchlorate fractions was determined. The fractions were separated and the chlorate and perchlorate fractions were reduced to chloride. Each fraction was precipitated in the form of AgCl for counting. Contaminating S35 activity was removed by dissolving the precipitates in aqueous ammonia and reprecipitating with nitric acid in the presence of sodium sulfate holdback carrier. The percentages of the total Cl<sup>36</sup> activity found in each fraction are given in Table I. Corrections have been made for the thickness of the sample by means of an empirical calibration curve.

It is evident from the analytical results given in Table I that considerable decomposition of the sodium chlorate has taken place, with a net loss of oxygen from the sample. This decomposition is almost certainly due to chemical reactions resulting from the intense gamma radiation to which the samples were exposed.

Table I also shows the ratio of the activities per mole of the three substances present in the irradiated samples. The results indicate that under the conditions of this experiment, production of Cl<sup>36</sup> in the chloride form takes place to give a specific activity only 21 times greater than the specific activity of the sodium chlorate. The apparent retention of the Cl36 activity in the form of sodium chlorate is 12.7 percent which is larger than the retention following the  $Cl^{37}(n,\gamma)Cl^{38}$  or the  $Cl^{35}(\gamma,n)Cl^{34}$  reactions in the same compound. The higher value is probably due to the reverse of the reaction which produces the large amount of sodium chloride under the influence of gamma rays. It has been shown<sup>3</sup> that when bromates are exposed to pile radiation, considerable back reaction does take place.

The Clas activities per mole of the chlorate and perchlorate fractions are equal within experimental error. It appears likely that the sodium perchlorate is produced during the irradiation from direct oxidation of sodium chlorate, rather than by oxidation of the sodium chloride.

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#### Low-Temperature Specific Heats of Vitreous and Crystalline Silica

M. DANK AND S. W. BARBER

General Research Division, Owens-Illinois Glass Company, Toledo, Ohio (Received December 28, 1954)

DECENT heat capacity measurements<sup>1</sup> on vitreous silica and X cristobalite can be fitted between 5° and 30°K by,

$$C_{v} = \frac{C_{2}\left(\frac{\theta_{2}}{T}\right) - y^{2}C_{2}\left(\frac{\theta_{3}}{T}\right) + y^{3}C_{3}\left(\frac{\theta_{3}}{T}\right)}{1 - y^{2} + y^{3}}$$
(1)

$$C_{2}\left(\frac{\theta_{n}}{T}\right) = 6R\left(\frac{T}{\theta_{n}}\right)^{2} \int_{0}^{\theta_{n}/T} \frac{x^{3}e^{x}dx}{(e^{x}-1)^{2}}$$
$$\theta_{n} = \frac{h\nu_{n}}{k}; \quad x = \frac{h\nu}{kT}$$
$$y = \frac{\theta_{2}}{\theta_{2}} = \frac{\nu_{3}}{\nu_{2}}.$$

Equation (1) is a modification of a function originally proposed by Tarassov.2,3

The function  $C_2(\theta_n/T)$  represents the heat capacities of idealized two-dimensional continua, while  $C_3(\theta_n/T)$  is the well-known Debye function. The characteristic temperature  $\theta_2$  is assumed to correspond to the maximum,  $\nu_2$ , of a class of frequencies consisting of translations normal to the "layer" and rotational oscillation about axes n the "layer," while  $\theta_3$  is assumed to correspond to a maximum,  $\nu_3$ , in a class of relatively low frequencies which, because of interactions between "layers" in real laminar solids, are characteristic of isotropic solids. The coefficients  $y^2$  and  $y^3$  are required to make all the terms in Eq. (1) refer to the same volume of material and division by  $(1-y^2+y^3)$  is required to adjust the function to the 3R limit.

It was found that  $\theta_2$  can be estimated from the temperature dependence of the heat capacities of vitreous silica per gram-atom between 8° and 20°K which leads to  $\nu_2 \sim 350 \text{ cm}^{-1}$ . This frequency is too low to be associated with atom-atom vibration, and at temperatures above 30°K, calculated heat capacities [using Eq. (1)] based on it are considerably higher than observed values. Even an assumed mass unit SiO<sub>2</sub> results in  $\nu_2 \sim 200 \text{ cm}^{-1}$  and also leads for  $T>30^{\circ}$ K to calculated heat capacities larger than those ob-

where

served in spite of known contributions from atom-atom vibrations in the experimental values. This situation requires the choice of mass units larger than SiO<sub>2</sub>. It was found that the heat capacity of vitreous silica per Si<sub>3</sub>O<sub>6</sub>, a mass unit used by Saksena<sup>4</sup> in his discussion of quartz, leads to  $\nu_2 = 115$  and  $117 \text{ cm}^{-1}$  for samples stabilized at 1070° and 1300° respectively, values close to the infrared frequency 116 cm<sup>-1</sup> observed by Barnes<sup>5</sup> at room temperature. A similar treatment of the data on cristobalite yields  $\nu_2 = 113$  cm<sup>-1</sup>, but there are no spectral data for comparison. Values of y for vitreous silica and cristobalite are 0.20 and 0.22, respectively. The experimental heat capacities (plotted points) of



cristobalite and vitreous silica as functions of  $T^2$  are compared with Eq. (1) (curves) in Fig. 1. Calculations of  $\nu_2$  from slopes of the indicated linear regions of the curves yield the above values within about 4 cm<sup>-1</sup>.

Various functions<sup>3</sup> similar to Eq. (1) have been derived theoretically for known layer-like solids such as graphite.<sup>6</sup> These new observations on silica, therefore, suggest the existence at low temperatures of highly anisotropic structures for cristobalite and vitreous silica both of which have been regarded as isotropic on the basis of x-ray studies and the macroscopic isotropy of various physical properties. Vitreous silica has long been regarded, on the basis of x-ray studies,<sup>7</sup> as a continuous silicon-oxygen network with close-range order no greater than about 8A. The anisotropy implied here seems to require more extensive order in accord with light scattering<sup>8</sup> and electron microscopy<sup>9</sup> experiments.

The heat capacity data for quartz revealed no evidence of molecular-scale anisotropy.

A detailed analysis and a new five-decimal place table of corrected values for  $C_2(\theta/T)$  will be submitted shortly for publication

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### Lowest Singlet Excited Levels of Naphthalene

CARL M. MOSER, Pavillon Pasteur, Institut du Radium, 11 rue P. Curie, Paris V, France

AND

ROLAND LEFEBVRF, Centre de Chimie Théorique, 155 Rue de Sèvres, Paris XV, France (Received December 10, 1954)

HERE has recently been considerable interest in the polarization of the lowest singlet electronic levels of naphthalene both from the experimental and theoretical point of view.<sup>1-7</sup> We have been interested in the problem for some time and briefly report our findings here.

Our calculations have been based on the usual " $\pi$ -approximation," and the method of evaluating the molecular integrals is very similar to that suggested by Pariser and Parr.<sup>8</sup> We have considered only a limited amount of configuration interaction, taking into account the two lowest configurations in each of the classes  ${}^{1}B_{1u}$  and  ${}^{1}B_{2u}$ . With this restriction, when using cyclic orbitals there is an easy, direct relationship with the configurations built to resemble the benzene configurations.

As starting orbitals for the calculations the usual Hückel orbitals, cyclic orbitals, and SCF orbitals,9 which are pertinent to the procedure of evaluating the integrals have been used. In each case the first transition has been found to be polarized along the long axis of the molecule  $({}^{1}B_{1u})$  and the second transition along the short axis of the molecule  $({}^{1}B_{2u})$ . It is of particular interest to note that this limited amount of configuration interaction provides for a considerable diminution of the calculated value of the intensity of the first transition as compared to the value of the intensity calculated from individual configurations built on Hückel-like orbitals. There appears to be very clear further evidence that in ad hoc interpretation of electronic spectra one cannot assume that a very weak transition is necessarily forbidden.

This method for the explicit evaluation of integrals gives the opportunity to follow the ideas on the modifications of semiempirical calculations recently suggested by Dewar and Longuet-Higgins<sup>7</sup> and by Moffitt.<sup>6</sup>

When following the outline given by Dewar and Longuet-Higgins<sup>7</sup> there is no essential difference in the mixing of the configurations of symmetry  ${}^{1}B_{1u}$  and  ${}^{1}B_{2u}$ . Nothing appears in these calculations that would enable one to distinguish "first-order" and "second-order" configuration interaction.

The procedure of Moffitt<sup>6</sup> has been followed in which configurations from complex orbitals are built to resemble the benzene configurations.

The interaction of the configuration that would be zero if naphthalene were a truly cyclic molecule has been calculated. It will be well, perhaps, to recall here that if there is no mixing of these configurations it would imply an exact 50-50 mixing of the configurations built on real cyclic orbitals.

The results are in substantial qualitative agreement with those of Moffitt. Mixing is brought about by one electron core integrals and two electron repulsion integrals, and is more important in the  ${}^{1}B_{2u}$  than in the  ${}^{1}B_{1u}$  case. The single configurations built to resemble benzene are nonetheless considerably better than those built on Hückel-like orbitals.

The details of these calculations will be published elsewhere in due course.

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