and satisfactory analysis reported for this p-bromoanilide it is quite probable that it was contaminated with some of the ortho isomer, as it was prepared by the bromination of isobutyranilide. p-Bromoisovaleranilide does not appear to have been described previously in the literature.

CONTRIBUTION FROM THE   MARGUERITE KUEHN
DEPARTMENT OF CHEMISTRY   S. M. McELVAIN
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN
RECEIVED JANUARY 26. 1931
PUBLISHED MARCH 6. 1931

COMMUNICATIONS TO THE EDITOR

THE α,β,γ-TRIMETHYLGLUTARIC ACIDS

Sir:

In a recent paper Michael and Ross[1] reported the failure to obtain α,β,γ-trimethyl-α-carboxyglutaric acid in a crystalline form. I had obtained this acid[2] and reported it as melting at 144–145°. Michael and Ross note that 145° is also the melting point of α,β-dimethyl-γ-carboxyglutaric acid, which suggests that the two are identical. The fact is that I obtained α,β,γ-trimethylglutaric acid melting at 134° from the decomposition of my acid, whereas α,β-dimethyl-γ-carboxyglutaric acid upon decomposition gives α,β-dimethylglutaric acid melting at 87°.[3]

Michael and Ross obtained α,β,γ-trimethyl-α-carboxyglutaric acid as a sirup which on distillation gave an acid melting at 115–125°. In my work on these compounds I found that it was necessary to obtain the tricarboxylic acid in a pure state before decomposing it in order to effect the purification of the α,β,γ-trimethylglutaric acid. Even so it required ten recrystallizations to reach the melting point of 134°. The compound which Michael and Ross describe as *cis*-α,β,γ-trimethylglutaric acid, which according to their statement "softened at 115° and melted at 125°," was probably an impure acid identical with mine, which melted at 134°. The liquid which they call *trans*-α,β,γ-trimethylglutaric acid was, apparently, the same as the liquid remaining in the mother liquors from the crystallization of the acid melting at 134°. Neither their work nor mine is sufficiently complete to characterize this liquid as a definite chemical individual. Inasmuch as modern theory predicts the occurrence of *three* stereoisomeric forms (one racemic and two meso acids) it would, in my opinion, be unfortunate if it should be so described in handbooks.

Michael and Ross attempted to separate their acids into a *"cis"* and a *"trans"* form by converting the *"cis"* form into the anhydride and the imide. Granting free rotation about a single bond *all three* of the possible

[1] Michael and Ross, THIS JOURNAL, **52**, 4607 (1930).

[2] Ray, *ibid.*, **50**, 558 (1928).

[3] Thorpe, *J. Chem. Soc.*, **83**, 358 (1903).

compounds should form anhydrides or imides and no direct separation is possible by this method.[4]

DEPARTMENT OF CHEMISTRY   F. E. RAY
UNIVERSITY OF CINCINNATI
CINCINNATI, OHIO
RECEIVED DECEMBER 1, 1930
PUBLISHED MARCH 6, 1931

THE α,β,γ-TRIMETHYLGLUTARIC ACIDS

Sir:

In the preceding Communication F. E. Ray expresses the opinion that in our recent paper [THIS JOURNAL, **52**, 4598 (1930)] (a) certain compounds described were impure and (b) that the method of separation of the α,β,γ-trimethylglutaric acids was not valid.

With respect to his first objection, we would draw attention to the fact that the compounds we described were analytically pure and, in the cases where crystalline, were unchanged in melting points after the third crystallization.

Ray prepared his tiglic ester through methylethylmalonic ester, obtained apparently by methylation and ethylation of sodium enol malonic ester. Besides the methylethylmalonic ester, the reaction product would contain monomethyl or ethyl and dimethyl or diethyl malonic esters, which cannot be completely separated by fractional distillation [Michael, *J. prakt. Chem.*, **72**, 537 (1905)]. Ray finally obtained a product which boiled at 100° (30 mm.), which is clearly too high for tiglic ester (b. p. 156° (760 mm.)). The addition compound he prepared from this product through sodium enol cyanacetic ester boiled at 150–170° (30 mm.) and this obviously impure material was methylated. By hydrolysis the product gave a solid acid from which by repeated crystallization, a 145° melting acid was isolated. This was considered to be α-carboxy α,β,γ-trimethylglutaric

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[4] Since writing this Note, Michael and Ross in a footnote contained in the following Communication to the Editor, p. 1175, have kindly called my attention to a transposition of an analysis in my paper[5] [THIS JOURNAL, **50**, 562 (1928)]. The silver salt of α,β,γ-trimethyl-α-carboxyglutaric acid was analyzed and found correct (page 562, line 15). Following this is given the titration of the α,β,γ-trimethylglutaric acid, C_8-$H_{14}O_4$. This should, of course, have followed the paragraph which describes the preparation of this acid from the malonic acid derivative for which the analysis of the silver salt is given.

In the hope of identifying this α,β,γ-trimethylglutaric acid (m. p. 134°) as the racemic form I have attempted its resolution by means of the brucine and strychnine salts but without success. It may thus be one of the meso forms. As a check to previous work the silver salt of the acid was prepared and analyzed with the following results:

Anal. Subs., 0.0450: Ag, 0.0248. Calcd. for $C_8H_{12}O_4Ag_2$: Ag, 55.6. Found: Ag, 55.1.

This leaves no doubt that the acid melting at 134° is α,β,γ-trimethylglutaric acid.

acid but the formula was not proved by analysis.[1] No yield was given of this acid and it was not clear from the description in his paper that the 145° melting acid was used for pyrogenic decomposition. In his preparation of the tribasic acid through tiglic and sodium enol malonic esters, Ray obtained it as a sirup from which apparently he could obtain the 134° melting dicarboxylic acid more readily than from the 145° melting acid. It is therefore difficult to understand the reference in his letter of "necessity to purify before decomposition." The acid melting at 134° was described as α,β,γ-trimethylglutaric acid, although no analyses of this material are given. We, therefore, cannot attach the importance that Ray does to this substance of unknown composition, obtained from an impure source.

With respect to the second objection, the validity of the method is a well established fact. The stereomeric poly-alkyl dicarboxylic acids do not form anhydrides with equal facility, or of equal stability, and we refer Dr. Ray to the literature of these acids [Perkin and Bone, *J. Chem. Soc.*, **69**, 264 (1896); Thorpe and Young, *ibid.*, **83**, 358 (1903), and others].

Since we used this method in the separation of the α,β,γ-trimethylglutaric acids, our products were described as *cis* and *trans* to indicate their origin and relative ease of anhydride formation. It was not relevant to our investigation to separate the possible stereomeric forms of α,β,γ-trimethylglutaric acid; it was sufficient for us to obtain a pure imide, m. p. 90°, and an acid, m. p. 125°, as reference compounds and to indicate further the existence of a *trans* acid form.

CONVERSE MEMORIAL LABORATORY   ARTHUR MICHAEL
CAMBRIDGE, MASSACHUSETTS   JOHN ROSS
RECEIVED DECEMBER 18. 1930
PUBLISHED MARCH 6. 1931

STEREOCHEMISTRY OF DERIVATIVES OF DIPHENYL AND ANALOGS

Sir:

Apparently the first suggestion that stereoisomerism of the type observed in the diphenyl series might also occur among binuclear heterocyclic aromatic substances is due to Kermack and Slater,[1] who attempted the resolution of 3-o-nitrophenyl-indole-2-carboxylic acid. A recent publication by Steele and Adams[2] describes the attempted resolution of certain phenylpyridine compounds.

[1] Ray gives no C and H analysis of this acid. Using very small quantities of material he showed by analysis of the silver salt that the silver content agreed with the formula of a tricarboxylic acid $C_9H_{14}O_6$, but titration with 0.1 N alkali indicated a dicarboxylic acid $C_8H_{14}O_4$. Analysis of the silver salt and titration could only indicate the equivalent of the acid. These conflicting analyses cannot indicate whether the acid was methylated; that is, whether the acid was $C_9H_{14}O_6$ or $C_8H_{12}O_4$.

[1] Kermack and Slater, *J. Chem. Soc.*, 36 (1928).

[2] Steele and Adams, THIS JOURNAL, **52**, 4528 (1930).

An extensive investigation of such heterocyclic substances as might be expected to exhibit stereoisomerism of diphenyl type has been in progress in these laboratories for some time, but owing to failure to obtain the substances examined in enantiomorphous forms up to the present, publication of results, with the exception of an introductory paper by Chalmers, Lions and Robson,[3] has been so far withheld.

In the 2-phenylpyridine series and the 2-phenylquinoline series attempts have been made to provide a "blocking group" by conversion of the tertiary nitrogen atom into a quaternary salt. Thus, 2-(-o-carboxyphenyl-)-3-carboxypyridine methosulfate (I) has been examined. but its resolution not effected.
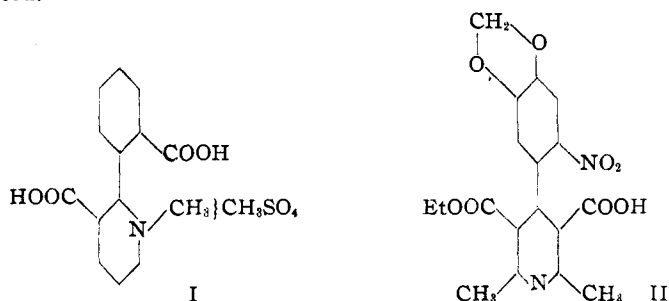
Derivatives of 4-phenylpyridine such as (II) have been prepared by the Hantzsch synthesis, and attempts at resolution are in progress. It is worthy of note in this connection that ortho-substituted benzaldehydes react least readily in the Hantzsch synthesis.[4] In the isoquinoline series 1-(-o-chlorophenyl-)-isoquinoline methiodide and ethiodide, and 1-(-o-tolyl-)-isoquinoline methiodide and ethiodide have been prepared and converted into the corresponding salts of optically active acids, but these are apparently homogeneous. The acridine compounds (III) and (IV) have also been prepared and examined but not separated into enantiomorphs.
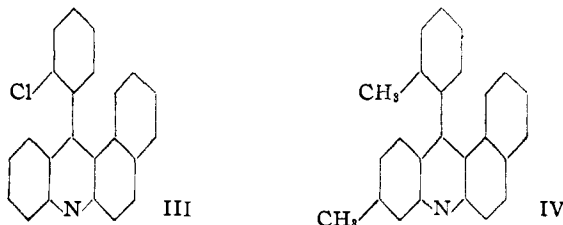

This consistent failure to resolve a compound of the phenylpyridine series suggests that the conditions there obtaining are different from those in the diphenyl series, probably owing to the definitely polar character of

[3] Chalmers, Lions and Robson, *J. Roy. Soc. New South Wales* (1930).

[4] Hinkel and Madel, *J. Chem. Soc.*, 750 (1929).

the pyridine nitrogen atom. Undoubtedly, there would be a powerful attraction between this atom and an ortho carboxyl of the benzene ring, leading to pronounced molecular distortion. As yet, the resolution of a derivative of diphenyl having strongly positive groups in the 2,2′-positions and strongly negative groups in the 6,6′-positions has not been effected. 2,2′-Diamino-6,6′-dicarboxydiphenyl (V) passes immediately on its formation into the dilactam (VI).[5] Presumably, in this substance both pyridone rings lie in the same plane as the benzene rings, though this has not definitely been established.
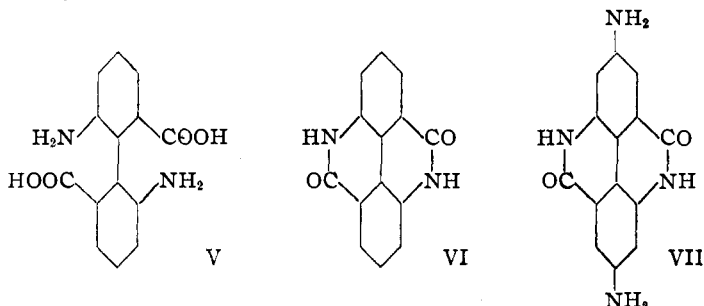

At present the optical homogeneity of (VII) is under examination. It is also proposed to attempt the preparation and resolution of ring homologs of (VI), e. g., the dilactam (VIII) in which the benzene rings should lie out of one plane, two configurations thus being possible. Further attempts to resolve 2,2′-tetramethyldiamino-6,6′-dicarboxydiphenyl (IX) and 2,2′-hexamethyldiamino-6,6′-dicarboxydiphenyl dimethiodide (X) and the corresponding betaine (XI) are in progress. The behavior of all these substances may shed some light on the phenomenon in the phenylpyridine series.
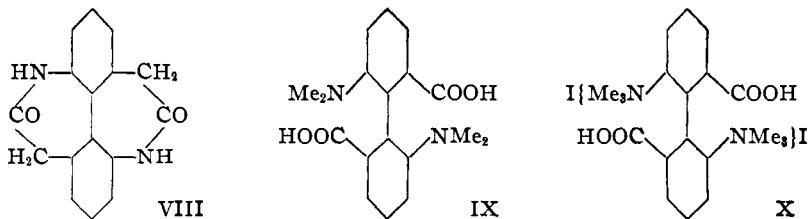
Finally, the examination of certain phenylpyrroles and phenylindoles is in progress. According to the obstacle theory it is to be expected that in such binuclear systems the smallest groups which would be effective in preventing free rotation of the nuclei about their common axis must be larger than in the diphenyl series. Hence, the first example chosen for study which is expected to be resolvable is 1-(-o-xenyl-)-2,5-diphenyl-pyrrole-3-carboxylic acid (XII).

5 Cf. Kenner and Stubbings, J. Chem. Soc., 119, 593 (1921).

XI   XII
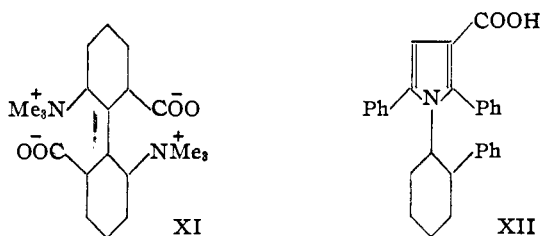
DEPARTMENT OF ORGANIC CHEMISTRY   FRANCIS LIONS
THE UNIVERSITY OF SYDNEY
NEW SOUTH WALES, AUSTRALIA
RECEIVED JANUARY 27, 1931
PUBLISHED MARCH 6, 1931

THE CRYSTAL FORM OF NICKEL OXIDES

Sir:

In making adsorption measurements of carbon dioxide on nickel oxide, it was found by one of us[1] that the adsorptive properties of the oxide varied quite markedly for different modes of heat treatment.

The nickel oxide was prepared by oxidation of suspended nickelous hydroxide with chlorine gas in basic solution. The black precipitate of the oxide was electrolyzed free of alkali and dried. One sample was outgassed several times at 285°, while the other was not subjected to a temperature of more than 110°.

The first preparation was the poorer adsorbent for carbon dioxide. The adsorption was carried out at 56.5° and the amounts adsorbed were in the approximate ratio of 1:2.5.

This difference of behavior, which was unlikely due to sintering, since the overheated form had rather smaller particle size as indicated by the line-width of the x-ray diagrams referred to below, also could not be explained on the basis of chemical differences, since in the Bunsen test for higher oxides, only traces of such could be found in either case. Both samples corresponded to nickelous oxide.

The substances were then subjected to x-ray analysis by means of the Debye–Scherrer–Hull method.

The overheated oxide corresponded exactly to the previously reported structure for nickelous oxide, being face-centered cubic. The edge of the unit cube was found to be 4.14 Å. (uncorrected), which corresponds to 4.17 Å. as given by the "International Critical Tables."

The structure of the nickelous oxide which had not been heated above 110° was quite different. Although also cubic, the edge of the unit cube was 4.64 Å. (uncorrected). The density was determined as 4.8 as compared to 6.69, given as the density of the ordinary nickelous oxide (Landolt–Börnstein "Tabellen"). The number of molecules in the unit cell

[1] O. G. Bennett, "Thesis," The Johns Hopkins University, 1930.

was calculated as four, with the same accuracy as for the known oxide. However, from a consideration of the intensities of reflection, the face-centered cubic type is not permissible. The complete determination of the atomic coördinates has not been finished as yet.

This form also differs from the ordinary nickelous oxide by causing an unusual amount of fogging on the photographic film when a Debye–Scherrer diagram is taken (Fe-radiation).

Evidently we have found a new cubic modification of nickelous oxide; we have also some evidence for the existence of further modifications. The possibility of the existence of several modifications of nickelous oxide is indicated by the work of Hedvall [*Z. anorg. Chem.*, **92**, 381 (1915)].

This work is being continued and special emphasis is laid on the determination of a possible relation between adsorption, catalysis and structure.

DEPARTMENT OF CHEMISTRY   O. G. BENNETT
THE JOHNS HOPKINS UNIVERSITY   R. W. CAIRNS
BALTIMORE, MARYLAND   EMIL OTT
RECEIVED JANUARY 28, 1931
PUBLISHED MARCH 6, 1931

THE FREE ENERGY OF FORMATION OF THALLIUM AMALGAMS

Sir:

Recently Tammann has reviewed the subject of heterogeneous equilibria both from the theoretical and the practical standpoint.[1] Besides describing the different types of phase diagrams, he shows how they can be derived from purely thermodynamic considerations, using the surfaces in free energy (F)–temperature–composition space taken for the several phases. Successive isothermal planes cut the F-surfaces in curves which define the singular points on isothermal lines across the phase diagram.

These surfaces, however, give only form and characteristics of the general types of diagrams, and have not been applied to any specific systems, since absolute values of F, which are needed for the calculation, have not been obtained, although changes of the free energy are easily measurable.

Nevertheless I believe I have succeeded in calculating a curve for the system thallium–mercury which represents the general form of the intersection of the free energy surfaces for that system with the 20° isothermal plane. I have calculated the free energy of formation of thallium amalgams from the elements, using the data of Richards and Daniels,[2] Lewis and Randall,[3] and Richards and Smyth[4] by a method which I will explain

[1] Tammann, "The States of Aggregation," translated by Mehl, D. Van Nostrand Co., New York, 1925; Tammann, "Metallography," translated by Dean and Swenson. The Chemical Catalog Co., New York, 1925; Tammann, "Lehrbuch der Heterogenen Gleichgewichte," Vieweg and Son, 1924.

[2] Richards and Daniels, THIS JOURNAL, 41, 1732 (1919).

[3] Lewis and Randall, *ibid.*, 43, 233 (1921).

[4] Richards and Smyth, *ibid.*, 44, 524 (1922).

in detail in the full report.   Briefly, the free energy of formation is a linear function of the mole fractions and partial molal free energies of thallium and mercury in amalgamated and free states.   If the last-named quantities—partial molal free energies of solid thallium and liquid mercury—were known, the true F-curve could be drawn; they are, however, constants at any given temperature, and enter my equations as products by the first power of the mole fraction, hence the only effect on the F-curve is to subject it to that type of linear transformation known as a "shear." While a "shear" will change certain features of a curve, such as slope, certain other features, in this case more important, are unchanged.   The curve is presented (Fig. 1).
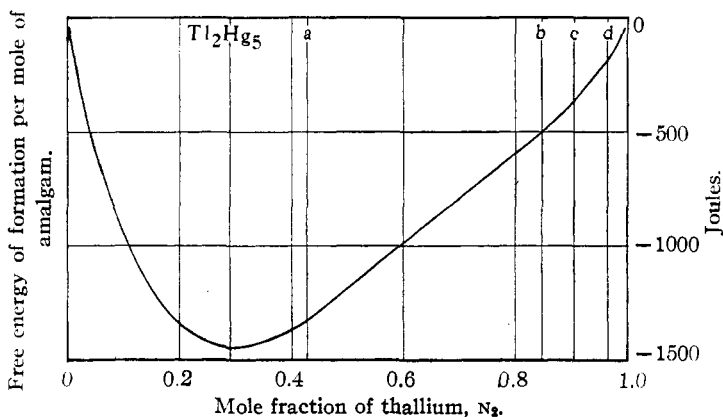

Fig. 1.—Free energies of formation of thallium amalgams.

The parts of the curve included between the vertical lines a and b, and c and d are straight lines, and will remain straight lines after a shear. Straight lines are to be expected, representing the common tangent to the free energy curves of the two phases in equilibrium in these regions.   There is also a minimum at $N_2 = 0.285$ which is not to be expected from Tammann's treatment.   It coincides, however, with the composition of the known compound Tl_2Hg_5.   The appearance of this minimum is all the more surprising since no singular point appears in the e. m. f. curve at this composition, and 20° is five degrees above the melting point of the compound, so that we have it existing in solution only.

Complete details of the method and calculations will be presented in an article to be submitted shortly.

RESEARCH LABORATORY OF   CHARLES EDWIN TEETER, JR.
INORGANIC CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS

THE OSCILLATING, PUCKERED, CENTROID MODEL FOR THE BENZENE RING

Sir:

Some time ago[1] the writer showed that many of the peculiarities of benzene and its derivatives could be accounted for by assuming a structure for the ring like that postulated by Körner[2] (Fig. 1, A) except for distorted (B) rather than regular tetrahedra. (The tetrahedra represent assumed preferred orientations of valence electrons or orbits.)[3]

The chief argument against this structure was lack of evidence for isomers which would be expected of disubstituted benzene derivatives. It has since been shown[4] that predictions on the basis of that theory that so-called 1,8-disubstitution products of naphthalene would be found to be 1,5-, and *vice versa*, are incorrect. Moreover, x-ray studies of graphite[5] and of $C(CH_3)_6$[6] have indicated that in these substances the centers of the carbon atoms, of a single layer or molecule, lie in or nearly in one plane.
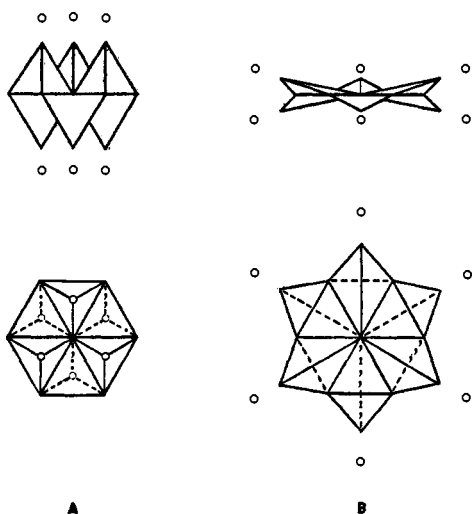
This evidence is satisfied if one assumes that the "tetrahedra" are sufficiently distorted, placing 1,8-substituents in naphthalene closer together than 1,5-substituents, and that there is frequent or constant oscillation between such a puckered form and its mirror image, preventing the isolation of isomers and giving a time-average distribution of x-ray scattering power ("electron density") like that deduced from the observations.

Consideration of such forces as the repulsion between atomic kernels would lead one to expect a tendency toward a puckered rather than a plane ring. With only slight puckering the same factors which are responsible for molecular rotation in the solid state[7] might be expected to

[1] Huggins, THIS JOURNAL, 44, 1607 (1922).

[2] Körner, *Gazz. chim. ital.*, 4, 444 (1874).

[3] *Cf.* Bartlett, *Phys. Rev.*, 36, 1096 (1930), and papers by Bartlett and by Slater at the Cleveland Meeting of the American Physical Society.

[4] Fuson, THIS JOURNAL, 46, 2779 (1924); 47, 2018 (1925).

[5] Hassel and Mark, *Z. Physik*, 25, 317 (1924); Bernal, *Proc. Roy. Soc.* (London), A106, 749 (1924).

[6] Lonsdale, *Proc. Roy. Soc.* (London), A123, 494 (1929).

[7] Pauling. *Phys. Rev.*, 36, 430 (1930).

produce the type of oscillation suggested. At sufficiently low temperatures this oscillation should cease. One would expect, therefore, small "humps" in the heat capacity curves of all benzene derivatives (unless oscillation is prevented by external forces), similar to those found[8] for certain of them which have been attributed[7] to rotation of CH_3 groups.

Another alternative is to assume easy (not necessarily frequent) oscillation and that the orientation of the puckering in a particular molecule in crystalline $C(CH_3)_6$ does not depend on the orientations in surrounding molecules.

The "anomalous" isomerism found among biphenyl derivatives may perhaps be due to non-oscillating puckered rings, rather than to a lack of free rotation about the bond joining them.

X-Ray studies have revealed no cases of two mutually perpendicular planes of symmetry passing through benzene ring centers (as would be expected if the rings were plane), although in several cases a center of symmetry has been found.[9] X-Ray evidence also definitely favors models with equivalent atoms at or oscillating about the corners of a regular hexagon. A satisfactory model must account, moreover, for the synthesis of benzene derivatives, first by methods indicating 1,4-linkages and second, by simple ring closure of a conjugated system.[10] The writer knows of no model, other than that proposed here, which meets these requirements.

From this model one would predict that "electron density" calculations from accurate x-ray intensity data by the method of Fourier Series summations[11] would show the carbon atom "peaks" to be considerably elongated normal to the "plane of the ring."

DEPARTMENT OF CHEMISTRY   MAURICE L. HUGGINS
STANFORD UNIVERSITY
STANFORD UNIVERSITY, CALIFORNIA
RECEIVED FEBRUARY 11, 1931
PUBLISHED MARCH 6, 1931

GRADUAL TRANSITION IN CRYSTALLINE SODIUM NITRATE[1]

Sir:

Some interest has been elicited in recent years in gradual transitions in crystalline solids. In these transitions the heat capacity of the crystal alters abnormally over an extended range of temperatures, with a more or less well-defined temperature at which the heat capacity reaches a maxi-

[8] Huffman, Parks and Daniels, THIS JOURNAL. **52**, 1547 (1930).

[9] See, for instance, Hendricks, *Chem. Rev.*, **7**, 431 (1930).

[10] Ingold, *J. Chem. Soc.*, **121**, 1143 (1922).

[11] Duane, *Proc. Nat. Acad. Sci.*, **11**, 489 (1925); Havighurst, *ibid.*, **11**, 502 (1925); Compton, "X-Rays and Electrons," D. Van Nostrand Co., Inc., New York, 1926, p. 151; W. L. Bragg, *Proc. Roy. Soc.* (London), **A123**, 537 (1929).

[1] Abstract of a presentation made at the February meeting of the Washington Section of the American Chemical Society, Washington, D. C.

mum, but there is no sharply defined finite discontinuity in the total heat absorbed. All the examples quoted in the literature (see, *e. g.*, the work of F. Simon on ammonium salts, Giauque and Wiebe on hydrogen bromide and iodide, K. Clusius on crystalline nitrogen, oxygen, methane, etc.) occur in the region of very low temperatures, and are for this reason difficult to examine for changes in other physical properties. There exists accordingly some uncertainty as to the exact behavior of a crystal during these apparent inversions, and doubt has been expressed [A. Smits, *Physik. Z.*, (1930)] as to whether the experimental conditions do not account for the anomaly. It is also clear that theoretical explanations of this type of transition [L. Pauling, *Phys. Rev.*, August (1930)] cannot be fully accepted for all cases until our knowledge is more complete.

Sodium nitrate exhibits a gradual transition which ends at approximately 275°. We have examined the changes in heat capacity as shown by differential heating and cooling curves, thermal expansion, the solubility of the salt to its melting point in water, and the x-ray diffraction patterns at various temperatures. Further work on other properties is in progress. The results obtained indicate that the properties of sodium nitrate crystals alter reproducibly over a range of temperatures rather than suddenly at a definite transition point. The expansion coefficient is nearly constant to about 150°, then it gradually increases to a peak value near 275°, followed by a rapid decrease to a normal value beyond 280°. The heat absorption on heating likewise gradually increases to a maximum at 275.5°, while on cooling the heat evolution begins at about 278°. Hysteresis phenomena are completely absent. The change in x-ray patterns is definite but small, and optical examination with a heating microscope shows that the crystals remain optically uniaxial up to the melting point. The solubility curve undergoes a small, but apparently real, change in the transition region. The detailed results of the experimental work will be communicated in the near future.

THE GEOPHYSICAL LABORATORY   F. C. KRACEK
CARNEGIE INSTITUTION OF WASHINGTON   E. POSNJAK
WASHINGTON, D. C.
RECEIVED FEBRUARY 16, 1931
PUBLISHED MARCH 6, 1931

THE PHOTO-REACTION BETWEEN HYDROGEN AND IODINE MONOCHLORIDE

Sir:

In a note on the reaction between iodine monochloride and hydrogen, D. P. Mellor and T. Iredale[1] have presented some experiments which they believe are contrary to conclusions presented by us in a recent paper.[2]

[1] Mellor and Iredale, *Nature*, 127, 93 (1931).

[2] Rollefson and Lindquist, THIS JOURNAL, 52, 2793 (1930).

We wish to call attention to the fact that their experimental results are not a contradiction of ours, as the conditions were considerably different, and furthermore their results may be interpreted in a manner consistent with our conclusions.

In the first place if we have a group of normal chlorine atoms formed, approximately 2% of them should in time acquire the energy of activation to the $^2P_1$ state by collisions. These atoms would be capable of forming hydrochloric acid by reaction with hydrogen. If, however, the atoms were destroyed by a reaction such as $ICl + Cl = Cl_2 + I$ before they acquired this energy, there would be no hydrochloric acid formation. Therefore, the most favorable conditions for reaction with hydrogen would be with the hydrogen pressure much higher than the iodine monochloride pressure. Mellor and Iredale had this condition in that they had the hydrogen pressure approximately forty times that of the iodine monochloride, whereas in our experiments of this kind the two pressures were of the same magnitude. Our results were confirmed by Franck and Rabinowitsch,[3] who found no reaction between hydrogen and iodine monochloride when they used an electric spark for excitation.

Mellor and Iredale apparently missed the principal point of our argument, namely, that in a given mixture of iodine monochloride, chlorine and hydrogen, light absorbed by the chlorine started a reaction whereas that absorbed by the iodine monochloride did not. That experimental fact is definite proof that the action of light on chlorine gives a product different from that resulting from iodine monochloride. This point is discussed in detail in our previous paper.

DEPARTMENT OF CHEMISTRY   G. K. ROLLEFSON
UNIVERSITY OF CALIFORNIA   F. E. LINDQUIST
BERKELEY, CALIFORNIA
RECEIVED FEBRUARY 16, 1931
PUBLISHED MARCH 6, 1931

THE REMOVAL OF HYDROGEN HALIDE FROM ORGANIC HALIDES

Sir:

In view of the recent appearance of an article by Semb and McElvain [THIS JOURNAL, **53,** 690 (1931)] on the reaction of organic halides with secondary amines, we should like to state that we have been investigating the reaction of organic halides with tertiary amines with the hope of using this reaction to determine the relative ease of removal of hydrogen halide from various organic halides. From the work of Semb and McElvain it is apparent that the usual course of the reaction of organic halides with secondary amines, and in particular with piperidine, is the formation of tertiary amines and that the removal of hydrogen halide takes place to a considerable extent only from tertiary halides. In our work using

[3] Franck and Rabinowitsch, *Z. Elektrochem.*, **36,** 794 (1930).

tertiary amines, and in particular pyridine, the main reaction other than quaternary salt formation appears to be the removal of halogen acid, although rearrangement of the quaternary salt to alkyl pyridine hydrohalides has not been excluded. We have used direct titration with standard alkali to determine the extent of elimination of hydrogen halide and have followed the rate of this reaction for a number of alkyl halides. We hope to be able to publish our results shortly.

DEPARTMENT OF CHEMISTRY   C. R. NOLLER
STANFORD UNIVERSITY, CALIFORNIA   R. DINSMORE
RECEIVED FEBRUARY 24, 1931
PUBLISHED MARCH 6, 1931

CALCULATIONS ON THE VELOCITY OF SOUND IN NITROGEN TETROXIDE

Sir:

In a recent publication, Kistiakowsky and Richards[1] describe an attempt to determine the velocity of the dissociation of nitrogen tetroxide from measurements of the velocity of sound in the gas at 25° and various pressures. Their experimental curve for the change in velocity with pressure is not in good agreement with that calculated from the equation of Einstein[2] giving the velocity of sound in a dissociating gas at frequencies below the critical frequency. Kistiakowsky and Richards attribute the deviation to the inaccuracy of the dissociation data of Bodenstein[3] used in the calculations.

In a forthcoming publication, we report new data on the dissociation of nitrogen tetroxide; we have substituted these data in the theoretical equation and compared the result with the curves of Kistiakowsky and Richards. Einstein's derivation assumes that the gas in question is a perfect gas; this is obviously not true for nitrogen tetroxide. Since we have the pressure coefficient of the equilibrium constant, which varies at 25° according to the equation

$$K_p = 0.1426 - 0.7588 \ C^0_{N_2O_4}$$

where

$$C^0_{N_2O_4} = \frac{\text{weight of } (N_2O_4 + NO_2)}{92.02}$$

we can calculate, for any given pressure, the deviation from the ideal condition. Further, from our extrapolation to zero pressure, we have a new value for the heat of dissociation—13,960 calories per mole at constant volume. In making the calculations, we have accepted the values assumed by Kistiakowsky and Richards for the specific heats of nitrogen tetroxide and nitrogen dioxide.

We have plotted the velocity of sound, $V_{\text{theoretical}}$, as calculated from

[1] Kistiakowsky and Richards, THIS JOURNAL, **52**, 4661 (1930)
[2] Einstein, *Sitzb. Berl. Akad.*, 380 (1920).
[3] Bodenstein, *Z. physik. Chem.*, **100**, 68 (1922).

our dissociation data, on a graph similar to that given by Kistiakowsky and Richards on page 4666 (Reference 1). The differences between this curve and the curve representing the direct experimental measurements of Kistiakowsky and Richards $V_{experimental}$ are given in the second column of the following table. In the last column are given the differences based on Bodenstein's data without the pressure corrections for the equilibrium constant.

Pressure in mm.	$V_{experimental} - V_{theoretical}$ (in meters/sec.)	
	Verhoek and Daniels	Bodenstein
200	2.9	2.2
300	3.0	1.2
400	2.9	0.7
500	2.4	.1
600	·1.9	− .3
700	1.5	− .7

While the agreement between the experimental curve and the theoretical curve can hardly be said to be any better using our data, the deviation is nearly constant, and the calculated velocity is always less than the observed velocity. This fact seems to indicate some constant error, either in theory or experiment. In the derivation of Einstein it is assumed that the gas is only slightly absorbing and that the dissociation proceeds according to a unimolecular reaction. It is possible that these assumptions are not sufficiently well satisfied.

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NEW BOOKS

Periodisches System. Geschichte und Theorie. (Periodic System: History and Theory.) By DR. EUGEN RABINOWITSCH, Göttingen, and DR. ERICH THILO, Berlin. Verlag von Ferdinand Enke, Stuttgart, Germany, 1930. xii + 302 pp. 50 figs. 16.5 × 24.5 cm.

This is a textbook which takes up the periodic system both from a chemical and physical point of view. It is a welcome addition to our list of textbooks as it collects in one place a considerable amount of related material of great importance to the chemist who is at all interested in theoretical things, and which, as far as the reviewer is aware, has not previously all been brought together in one place in textbook form. It is to be recommended for advanced students of chemistry who wish to (or ought to) learn something about quantum theory (even though it be mostly old quantum theory) and its applications, without wading through too much material of a highly mathematical character. But many people to whom most of the material is already familiar will undoubtedly be glad to find it