For the solvents used in Fig. 4, the temperature coefficients of the dielectric constants are negative and become smaller at the higher temperatures. This would tend to cause the conductance to be less at the higher temperatures and to influence the temperature coefficient of conductance less at the higher temperatures. For these same solvents the temperature coefficients of viscosity are negative and have smaller values at higher temperatures. This would cause an increase of conductance with increasing temperature but the rate of increase should be less at higher temperatures. Even though these two solvent properties work in opposition to each other, they both favor a smaller temperature coefficient at higher temperatures.

Preliminary work on the conductances of magnesium and barium chlorides gave curves of the same general form as those for strontium chloride.

## Summary

The conductances of strontium chloride and of strontium bromide in different ethanol–water mixtures have been measured at 25° and the significance of the results discussed.

The conductance of strontium chloride in different ethanol–water mixtures has been measured at 20, 25 and 30° and the temperature coefficients evaluated.

In strongly aqueous solutions the conductances are influenced mostly by the viscosity of the solvent and in the strongly alcoholic solutions mostly by the dielectric constant of the solvent.

EAST LANSING, MICHIGAN RECEIVED JANUARY 23, 1948

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

# Repulsive Forces in Relation to Bond Energies, Distances and Other Properties

BY KENNETH S. PITZER

While the concepts of quantum theory have given a qualitative understanding of most chemical bond phenomena, there are a number of less prominent features that remain puzzling. Many of the ideas in this paper have been held by the writer and very likely by others for some time. However, they were based on conflicting and uncertain data. The immediate reason for this paper is the recent developments in dissociation energy data which makes possible a greatly improved and considerably changed table of bond energies.

**Bond Energies.**—Gaydon[1] has recently published a very fine compilation of dissociation energies. Furthermore his recommended value of *ca.* 170 kcal. for the heat of sublimation of carbon (to normal $^3P$ atoms) has been fully confirmed by new thermodynamic measurements of Brewer and Gilles[2] in this Laboratory. The heat of vaporization values of Kelley[3] together with some revisions of these values by Brewer[4] have been employed. These new data supplement the older values of Bichowsky and Rossini[5] upon which Pauling[6] based most of his bond energies. The conventions followed in Tables I and II follow Pauling's system except that the dissociation energies of the nomal $^3\Sigma$ states rather than excited singlet states are taken for O═O, S═S, etc. The energy of dissociation of a molecule completely into atoms is taken as the sum of the energies of all bonds. Thus the C–H bond energy is not the energy change of the reaction of $CH_4 = CH_3 + H$ but rather one fourth of the energy for $CH_4 = C + 4H$. The values are for 0°K. Heat capacities from 0 to 300°K. were estimated where necessary.

In Table I there are listed values for single bonds in elements and for single bonds to hydro-

TABLE I

SINGLE BOND ENERGIES (KCAL./MOLE AT 0°K.)

| Elements | | Hydrides | | Chlorides | |
|---|---|---|---|---|---|
| H–H | 103.2 | H–H | 103.2 | H–Cl | 102.1 |
| Li–Li | 26 | Li–H | 58 | Li–Cl | 118.5 |
| C–C | 80 (85) | C–H | 98.2 | C–Cl | 78 |
| N–N | 37 | N–H | 92.2 | N–Cl | 46 (?) |
| O–O | 34 | O–H | 109.4 | O–Cl | 49 |
| F–F | 50 (?) | F–H | 141 (?) | F–Cl | 60.3 |
| Na–Na | 17.8 | Na–H | 47 | Na–Cl | 97.7 |
| Si–Si | (45) | Si–H | 76 (?) | Si–Cl | 87 |
| P–P | (53) | P–H | 77 | P–Cl | 77 |
| S–S | 63 (?) | S–H | 87 (?) | S–Cl | 65 (?) |
| Cl–Cl | 57.1 | Cl–H | 102.1 | Cl–Cl | 57.1 |
| K–K | 11.8 | K–H | 42.9 | K–Cl | 101.4 |
| Cu–Cu | | Cu–H | 62 | Cu–Cl | 83 |
| Ge–Ge | (39.2) | Ge–H | ... | Ge–Cl | ... |
| As–As | (39) | As–H | 56 | As–Cl | 69 |
| Se–Se | (50) | Se–H | 67 | Se–Cl | 59 |
| Br–Br | 45.4 (53) | Br–H | 86.7 | Br–Cl | 52.1 |
| Rb–Rb | 11.1 | Rb–H | 39 | Rb–Cl | 101.0 |
| Ag–Ag | ... | Ag–H | 53 | Ag–Cl | 71 |
| Sn–Sn | (35) | Sn–H | ... | Sn–Cl | 76 |
| Sb–Sb | (42) | Sb–H | ... | Sb–Cl | 75 |
| Te–Te | (49) | Te–H | 59 | Te–Cl | ... |
| I–I | 35.6 (51) | I–H | 70.6 | I–Cl | 49.6 |
| Cs–Cs | 10.4 | Cs–H | 41 | Cs–Cl | 103 |

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(1) A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, London, 1947.

(2) L. Brewer and P. Gilles, unpublished data.

(3) K. K. Kelley, U. S. Bureau of Mines, Bulletin 383, 1935.

(4) L. Brewer, "The Thermodynamic and Physical Properties of the Elements," Declassified Atomic Energy Report CC 2058, 1945.

(5) F. R. Bichowsky and F. D. Rossini, "Thermochemistry of Chemical Substances," Reinhold Pub. Co., New York, N. Y., 1936.

(6) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

TABLE II

MULTIPLE BOND ENERGIES (KCAL./MOLE AT 0°K.)

| | Single | Double | Triple |
|---|---|---|---|
| C–C | 80 | 145 | 198 |
| N–N | 37 | ... | 225.1 |
| O–O | 34 | 117.2 | ... |
| P–P | (53) | ... | 116.0 |
| S–S | 63 (?) | 101 (?) | ... |
| As–As | (39) | ... | 90.8 |
| Se–Se | (50) | 65 | ... |
| Sb–Sb | (42) | ... | 69 |
| Te–Te | (49) | 53 | ... |
| C–N | 66 | ... | 209 |
| C–O | 79 | 173 | ... |
| P–N | ... | ... | 138 (?) |
| S–O | ... | 120 (?) | ... |
| Te–O | ... | 62.8 | ... |

gen and chlorine. Table II gives values for multiple bond energies and includes the corresponding single bond energy for comparison. Naturally many more values could be included but these will serve as a basis of the discussion to follow.

In some cases the single bond energies for elements must be taken from solids where there may be additional weak bonding of a van der Waals or semi-metallic nature. Such values are inclosed in parentheses.

The first value given for the C–C bond is an average of several hydrocarbons.[7] It would be 77.7 for ethane but approaches 81.0 for higher and branched paraffins. The value from diamond, 85 kcal., is given in parenthesis. The values for N–N and O–O come from hydrazine and hydrogen peroxide on the basis of the values for N–H and O–H from ammonia and steam, respectively. The details for phosphorus will be typical of many other cases. The value for P≡P is from Gaydon.[1] Since the P–P bonds in $P_4$ are considerably strained, red phosphorus was taken as a basis. Bichowsky and Rossini give 29.1 kcal. for the heat of vaporization to $P_2$. Brewer gives 42 kcal. Adopting the latter, the heat of dissociation of two gram atoms of red phosphorus to atoms is therefore 42 + 116 = 158 kcal. Since this involves three bonds per two atoms the value for P–P is 53 kcal.

**Tetrahedral *vs.* p Orbital Bonding.**—The very pronounced drop in bond energy from C–C to N–N must be connected in some way with the appearance of the unshared electron pair on nitrogen. Tetravalent carbon must be based on the $2s2p^3$, $^5S$ state which is 96.4 kcal. higher in energy[8] than the normal $2s^22p^2$, $^3P$ state. Thus to the $^5S$ state the C–C bond energy would be 128 kcal., the C–H bond energy 122.3 kcal., etc. However, according to Bacher and Goudsmidt[9] the $2s2p^4$, $^4P$ state of nitrogen is 260 kcal. above the normal $2s^22p^3$, $^4S$ state. The large increase arises because in nitrogen the 2s electron is moved to a half filled 2p orbital whereas in carbon the 2s electron was moved to a vacant 2p orbital. If the trivalent nitrogen atom were to bond with $sp^3$ hybrid tetrahedral orbitals it would have to be excited $^3/_4$ of the way to the $2s2p^4$ state which would then amount to 65 kcal. extra per bond per atom. On this basis the N–N bond energy becomes 167 kcal. which is well above the value for C–C. However, it would seem more likely that the nitrogen bonding orbitals are mostly p with only a small s component. This avoids the large excitation energy but gives weaker bonds.[6] The less than tetrahedral bond angles in ammonia, etc., tend to confirm this picture. Presumably the normal valence bonding of all the 5th, 6th and 7th group elements is primarily p bonding since the bond angles for $PH_3$, $H_2S$, etc. approach the 90° value characteristic of p orbitals.

If the drop in bond energy at nitrogen is caused by the change to p bonds one is confronted by the absence of a corresponding drop from Si–Si to P–P. I believe this is closely related to the weakness of multiple bonds below the first row which will be considered next.

**Single and Multiple Bonds.**—It has long been recognized that multiple bonds of strength equal or greater than a corresponding number of single bonds occur only with the first row elements oxygen, nitrogen, carbon and possible boron. Only carbon disulfide and a few less clean cut examples show stable multiple bonds between first and second row elements. Multiple bonds with heavier atoms are confined to molecules such as $P_2$, $Se_2$, etc., which are of higher energy per atom than single bond structures $P_4$,$S_8$ etc.

Figures 1 and 2 indicate crudely the approximate size of various orbitals in nitrogen and phosphorus. The inner shells are given Pauling's "single bond" radii for $N^{+5}$ and $P^{+5}$, respectively. The outer radius is taken as 0.9 times the van der Waals radius also from Pauling.[6] The value of 0.9 was selected because it was felt the compressional forces within a molecule were rather larger than the intermolecular forces in a molecular crystal. The 2s orbital for nitrogen and the 3s for phosphorus were omitted to avoid confusion. Regions of bonding or attractive exchange overlap are diagonally cross hatched while the principal regions of repulsive exchange overlap are lined horizontally. The overlap of orthogonal orbitals such as $3p_x$ with $3p_z$ will have only a secondary effect. The atoms are shown at the bond distances experimentally observed.

It should be emphasized that orbitals do not have sharp boundaries and that Figs. 1 and 2 are therefore only crude representations. In particular the p orbitals gradually decreased in intensity from a maximum along their principal axis to zero in the plane perpendicular to that axis. They have been cut off at 44° from the axis to separate

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(7) E. J. Prosen, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 403 (1945).

(8) A. G. Shenstone, *Phys. Rev.*, **72**, 411 (1947).

(9) R. F. Bacher and S. Goudsmidt, "Atomic Energy States," McGraw Hill Book Company, New York, N. Y., 1932.

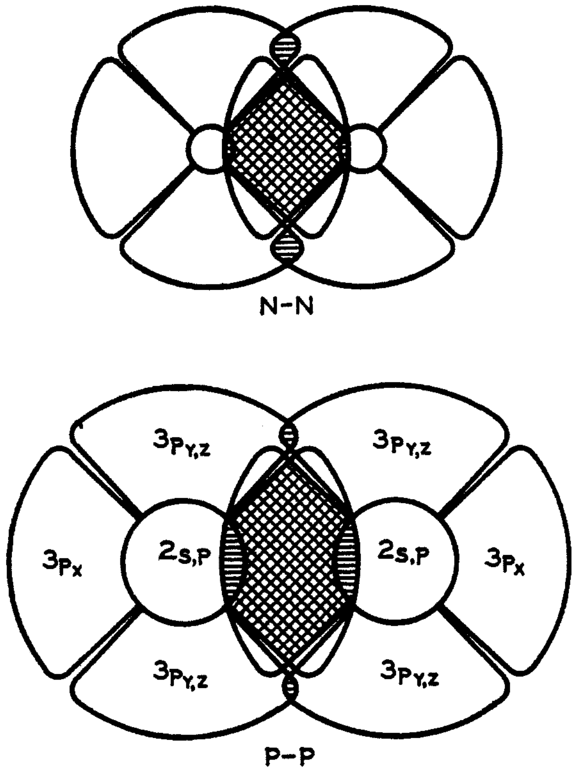


Fig. 1.—Diagrams of relative orbital sizes in N–N and P–P bonds.

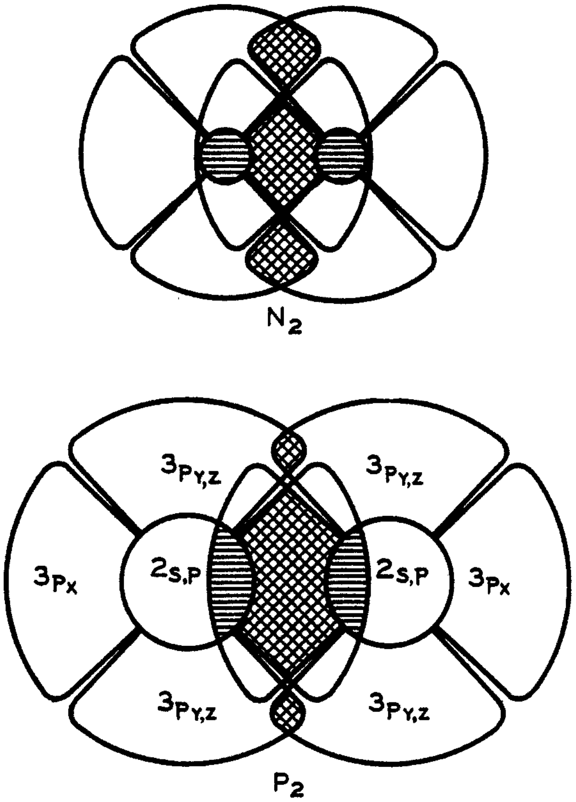


Fig. 2.—Diagrams of relative orbital sizes for N≡N and P≡P bonds.

the p orbitals on the same atom. Also since the intensity decreases both radially and angularly, the outer corners are of particularly low intensity. These corners rounded to remind one of this situation. In spite of their limitations the figures are useful in illustrating qualitative differences between nitrogen and phosphorus.

**Repulsive Effects of Inner Shells.**—In hydrogen the attractive force of the bonding electrons on the nuclei is balanced by the repulsive force of the two nuclei. However, in $P_2$ we postulate that the repulsive interactions of the $3p_x$ orbital of one atom with the inner shell of the other constitute a more important repulsive force. Let us call this merely *inner shell* repulsion. In nitrogen the inner shell contains only two electrons as compared to ten in phosphorus. Consequently it is reasonable to suppose that this inner shell repulsive effect is much smaller in nitrogen. These ideas receive support in Fig. 2 in that the N≡N bond distance is so short that the $2p_x$ orbital of one atom extends completely across and beyond the inner shell of the other while in P≡P the $3p_x$ orbital only partially overlaps the inner shell of the other atom. Since other interactions in $P_2$ are attractive there would appear to be no other reason why the distance should remain relatively longer than in $N_2$.

The increase in bond energy between the single and triple bonds comes from two principal sources. First, the interaction of the $p_y$ and $p_z$ orbitals changes from repulsive to attractive. Second, the bond distance decreases giving better overlap for all the bonding orbitals. If the $p_x$-inner shell repulsion keeps the bond distance large, both of these items are small. In the second case the reason is self-evident, and in the first it is because the $p_y$ and $p_z$ overlap is small at large distances. For double bonds the same argument applies but only the $p_y$ interaction is affected.

This inner shell repulsive effect will be general for all atoms below the first row. Consequently it will explain the relative weakness of multiple bonds for all atoms outside the first row. Next let us see if it will help account for other peculiarities.

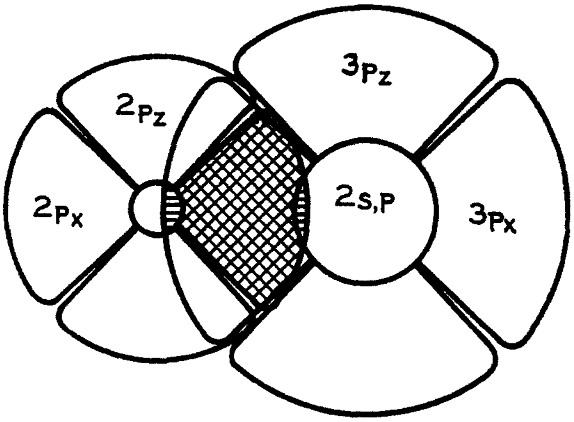
Pauling[6] suggests that p bonds should have $^3/_4$ of the energy of tetrahedral whereas we find a much smaller value for the ratio of N–N to C–C bond energy. However, Pauling's value may be interpreted as the ratio of the attractive energies of the bonding electrons alone. The net bond energy will be less by the repulsive effects of non-bonding interactions. We see in Fig. 1 that there is a considerable overlap of the $2p_z$ (and $2p_y$) orbitals which is repulsive. A shift to tetrahedral orbitals would decrease this greatly because of the increase from 90° to 109.5° in the angle between orbital axes. Thus one concludes that in the first row elements, single bonds with p orbitals are weaker than with tetrahedral orbitals because of increased repulsive interactions. Let us call these *valence shell* repulsions.

In heavier elements than the first row, however, we have assumed that the inner shell repulsions are important. Consequently, the valence shell repulsive effect will be less important. There is another factor to be considered here. The character of bonding orbitals may be modified by linear combination with any vacant orbitals, although only those of approximately the same energy can be important. Thus while the 3d orbitals could have only a minor effect for first row elements, the orbitals of second row elements may be considerably modified. The electron density will be concentrated more along the bond axis and will not spread out so far to each side. This change means that the $p_y$ and $p_z$ orbitals which are forming other single bonds perpendicular to the one shown in Fig. 1 will overlap even less than indicated there. Thus the absence of a marked drop in bond energy from Si–Si to P–P is also understandable.

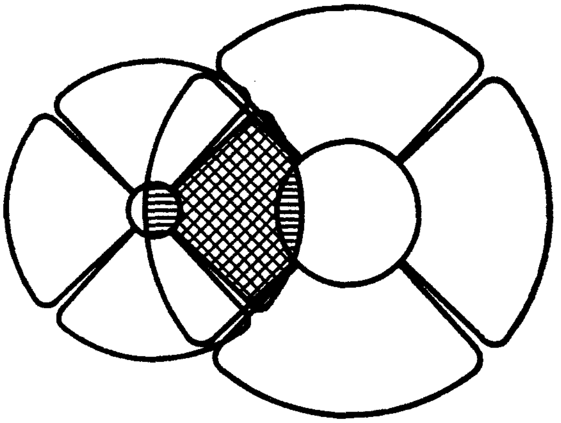
**Bond Distances.**—While the concept of covalent bond distances as sums of radii is undoubtedly but a first approximation, it has met with considerable success. Schomaker and Stevenson[10] modified this simple concept for partial ionic bonding effects and have found generally improved agreement. The major failure which remained was the series of bonds Si–O, P–O, Si–F and P–F (together with S–O in $SO_4^=$, Cl–O in $ClO_4^-$, etc.). These bonds are shorter than expected by about 0.10 Å. on the Schomaker and Stevenson formula and by 0.12 to 0.27 Å. on the Pauling and Huggins[11] scale.

Pauling[6] explains these effects as due to multiple bonds using 3d orbitals, but the writer has never regarded this acceptable because it is entirely *ad hoc* and without confirmation from energies and other sources. Also logical extensions of Pauling's structures lead to absurdities such as diatomic argon with the structure: $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{A}} = \underset{\cdot\cdot}{\overset{\cdot\cdot}{A}}:$.

Now it has been postulated in this paper that the N–N and similarly the O–O and F–F distances are determined largely by the valence shell ($2p_y$, $2p_z$) repulsion while the Si–Si, P–P, and S–S distances are determined principally by the repulsive interaction of the inner shell with the $3p_x$ orbital (or the tetrahedral hybrid in silicon). The basic radii are taken as half of the single bond distance with like atoms. However, when a phosphorus atom approaches an oxygen atom, for example, neither of these repulsive effects sets in at the distance calculated from the radii because of this difference in type of predominant repulsion. This is shown clearly in Fig. 3 which depicts P–O on the same basis as Figs. 1 and 2. Thus the upper diagram shows the nuclei at 1.76 Å. as calculated by Pauling and Huggins. The $2p_x$ orbital of oxygen hardly more than touches the inner shell of phosphorus and the $p_z$ (and $p_y$) orbitals have not overlapped partly because of the difference in atomic size. The $3p_x$ orbital of phosphorus overlaps the inner shell of oxygen but the latter contains only two electrons and was therefore regarded as less important.



D = 1.76 Å.



D = 1.64 Å.

Fig. 3.—Diagrams of the P–O bond at distances indicated.

The lower diagram in Fig. 3 shows the atoms at the distance 1.64 Å. observed in the $P_4O_6$ gas molecule. Even there the respulsive overlap of various orbitals is moderate. Furthermore the Si–O bond energy is quite normal. On Pauling's electronegativity formula, but using recent data, one calculates 106 kcal. for a single Si–O bond as compared to the observed 103 kcal. Data are not available for the normal P–O bond energy, but the values for Si–F are 159 kcal. calculated for a single bond and 138 kcal. observed. Thus the energies give no indication of multiple bonding.

In molecules such as $P_4O_{10}$ and $PO_4^{\equiv}$ even shorter bonds arise. While double bonds involving 3d orbitals are more likely in these cases than before, even here a formal charge explanation is equally reasonable. If one maintains the octet for phosphorus in $P_4O_{10}$ then the four oxygens which

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[10] V. Schomaker and D. P. Stevenson, This Journal, **63**, 37 (1941).

[11] L. P. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

are bonded to only one phosphorus have a net charge of −1 and the phosphorus atoms have a +1 charge. At the distance of about 1.6 Å. these charges give an attractive force of $9 \times 10^{-4}$ dynes. The force constant for a normal P–O single bond is not known but may be expected to be about $4 \times 10^5$ dynes/cm. from comparison with other molecules. Thus the electrostatic attractive force may be expected to lower the bond distance by about 0.2 Å. which is roughly that observed.

From these considerations, it is the writer's opinion that in the oxygen and fluorine compounds with second row elements multiple bonding is not significant (in the sense of more than one pair of electrons shared between the two atoms). The short bond distances are explainable in terms of (1) the difference in type of repulsive effect predominating in P–P, etc., from that in O–O, etc., and (2) the large polar effects.

Thus although the 3d orbitals undoubtedly play a part in the detailed nature of the p or sp$^3$ bonds in second row elements, it appears that they are not available for additional bonds of significant strength.

**Barriers to Rotation about Single Bonds.**—The very simplest quantum mechanical theory of single bonds indicates no restriction of rotation of the two groups connected by the bond. Thus the experimentally determined barriers of 1 to 4 kcal. per mole must be related to some refinements of the simplest theory. In ethane, if the carbon atom orbitals are strictly sp$^3$ hybrids, only H–H interactions are affected by rotation and they are too small. However, if the carbon orbitals are concentrated just a little more along the C–H bond directions then these atoms are no longer axially symmetrical. The C–C bond is pulling the two carbons together against the repulsion of these C–H bond electrons. Consequently it is reasonable to assume this repulsion to be larger when the C–H bonds at one end line up with those at the other end and to be less when the C–H bonds are staggered. The stability of the staggered orientation is now well verified. Let us examine the consistency of the magnitude of the rotation restricting barriers listed in Table III with the concepts that the barrier arises from variation in the valence shell repulsion as defined above.

Whereas the axial symmetry of a carbon atom is disturbed by three hydrogens in ethane there are only two hydrogens on the nitrogen of methyl amine and one on the oxygen of methanol. Thus one might expect the barriers to decrease in the ratio 3 to 2 to 1. However, the decrease in bond angle from tetrahedral at the carbon to smaller values for nitrogen and oxygen should increase this repulsive effect. The series ethane, methylamine, methanol and the series propane, dimethylamine, dimethyl ether both show increase from carbon to nitrogen followed by decrease to oxygen in reasonable accord with these ideas.

TABLE III

POTENTIAL BARRIERS RESTRICTING INTERNAL ROTATION (KCAL./MOLE)

| | | | |
|---|---|---|---|
| $CH_3CH_3$[12] | 2.8 | | |
| $CH_3NH_2$[13] | 3.0 | | |
| $CH_3OH$[18] | 2.3 ± 1(?) | $CH_3SH$[14] | 1.5 |
| $(CH_3)_2CH_2$[16] | 3.4 | | |
| $(CH_3)_2NH$[13] | 3.5 | | |
| $(CH_3)_2O$[13] | 3.1 | $(CH_3)_2S$[15] | 2.0 |
| $(CH_3)_4C$[17] | 4.3 | $(CH_3)_4Si$[18] | 1.3 |

Unfortunately, barrier values for bonds between two second row elements are now available. They should be small because the valence shell repulsion is largely replaced by the inner shell repulsion discussed above. The situation for bonds between carbon and a second row element should be intermediate and the values in Table III are clearly consistent with this concept.

**Bonds to Hydrogen.**—Since hydrogen has no further electrons, there should be no electronic repulsion effects of the valence shell type. Consequently the bond energies should show greater regularity. Thus the decrease in bond energy from C–H to N–H is very small compared with that from C–C to N–N or from C–Cl to N–Cl.

**Conclusions.**—In a single bond between two first row elements the attractive force of the bond itself is balanced principally against the repulsion of the remaining valence shell electrons. Between two second row or heavier elements the repulsion between the bonding orbital and the inner shell becomes more important. These concepts are shown to give qualitative explanation for:

1. The relative absence of stable multiple bonds except with first row elements.
2. The striking drop in bond energy from C–C to N–N.
3. The failure of bond radii to correctly predict the Si–F, P–O and related bond distances.
4. The relative magnitude of barriers to internal rotation about single bonds.

Certain predictions are made.

It does not seem likely that presently feasible quantum mechanical calculations could do more than confirm these qualitative conclusions. However, more quantitative relationships of an empirical nature might be developed.

## Summary

A revised table of bond energies is calculated from recent sources.

The concept is introduced of a balance in a

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(12) K. S. Pitzer, *Chem. Rev.*, **27**, 39 (1940).

(13) J. G. Aston, *Ind. Eng. Chem.*, **34**, 514 (1942); *Chem. Rev.*, **27**, 59 (1940).

(14) H. Russell, D. W. Osborne and D. M. Yost, THIS JOURNAL, **64**, 165 (1942).

(15) D. W. Osborne, R. N. Doescher and D. M. Yost, *ibid.*, **64**, 169 (1942).

(16) K. S. Pitzer, *J. Chem. Phys.*, **12**, 310 (1944).

(17) K. S. Pitzer and J. E. Kilpatrick, *Chem. Rev.*, **39**, 435 (1946).

(18) B. L. Crawford, Jr., *J. Chem. Phys.*, **8**, 744 (1940).

chemical bond between attractive and repulsive forces both of electronic nature. In first row elements the repulsive effects for single bonds arise principally in the valence shell whereas for heavier atoms the inner shells play a predominant role. The ideas are shown to account for several peculiarities in bonding behavior.

BERKELEY, CALIFORNIA RECEIVED DECEMBER 22, 1947

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

# Susceptibility Isotherms for Supported Copper Oxide

BY P. W. SELWOOD AND NICK S. DALLAS

The purpose of this work was to examine the structure of supported copper catalysts by use of the magnetic methods previously described.[1] The present paper gives magnetic data on a series of copper–alumina catalyst systems, together with some X-ray and catalytic activity results.

## Experimental

**Preparation and Analysis of Samples.**—Pure $\gamma$-alumina of surface area approximately 200 sq. m./g. and magnetic susceptibility $-0.2 \times 10^{-6}$ at −190°, was impregnated with copper nitrate solution, then filtered, dried, and ignited at 390° for twenty-four hours. Twelve samples of supported copper oxide were thus made, ranging in concentration from 0.60 to 34.7% copper.

The several samples were analyzed by dissolving them in nitric acid and titrating by the standard iodide–thiosulfate method. One catalyst sample was prepared by multiple impregnation. The copper nitrate impregnating solution was adjusted so as to give a catalyst containing about 1% copper. After ignition this catalyst was reimpregnated and ignited. The process was repeated until the copper concentration reached 5.2%.

Most of the catalyst samples were examined in the reduced condition as well as oxidized. Reduction was carried out in hydrogen at 300° for twelve hours. No change was caused by raising the reduction temperature to 400°.

It is of interest to record that the oxidized catalyst systems were bluish-green in color at all lower concentrations. The reduced catalysts were all jet black.

During the course of these studies it became necessary to prepare some supported silver oxide on alumina. This was obtained by impregnating $\gamma$-alumina with dilute silver nitrate solution, followed by drying and ignition at 390°. The sample contained approximately 2% silver. This sample was reduced in hydrogen at 200°. It may be mentioned that the oxidized silver supported on $\gamma$-alumina is rapidly changed from white to brown by mere exposure to hydrogen well below room temperature.

The reduced forms of all catalysts were readily reoxidized in air at room temperature. The lower concentrations were handled in the absence of air, although the reduced copper could be stabilized to a fair degree by exposure to carbon dioxide.

**Catalytic Measurements.**—Comparison of catalysts containing varying proportions of copper was made by mechanically mixing all samples, except the lowest in copper, with $\gamma$-alumina so that all samples contained 3.2% copper. The catalytic measurements were not extended below that concentration. The reaction chosen was the dehydrogenation of isopropyl alcohol.

A pelleted catalyst sample containing 0.32 g. of copper in 10 g. of catalyst was placed in the reaction chamber. The catalyst was reduced in hydrogen at 400° for two hours. The temperature was then lowered and held at 225°. Redistilled isopropyl alcohol was fed over the catalyst at the rate of 32 cc. (liquid) per hour. Tests were continued for one hour, and three successive such one hour activity runs were made for each catalyst.

The gaseous product was collected and the volume measured. The liquid product was fractionated in a simple column and a rough analysis was thereby obtained for acetone, unconverted isopropyl alcohol and higher boiling products.

The several catalysts used for the activity tests are conveniently described in the following manner. Catalyst 3.2/10.3 means a sample containing 3.2% of copper but that this was obtained by mechanically mixing appropriate amounts of $\gamma$-alumina and a $CuO/Al_2O_3$ impregnate which contained 10.3% of copper. Four such catalysts were tested. These are thus designated as 3.2/3.2, 3.2/10.3, 3.2/13.3 and 3.2/22.9.

## Results

Table I shows the magnetic susceptibility at three temperatures for all the oxidized copper catalyst samples except that prepared by multiple impregnation. Samples containing less than 3% copper are discarded as being too dilute to permit accurate estimation of the susceptibility of the copper. Figure 1 shows the susceptibility isotherms calculated from the data of Table I.

TABLE I

MAGNETIC SUSCEPTIBILITY OF $CuO/Al_2O_3$ CATALYST SAMPLES

| Weight per cent. copper | $x \times 10^6$ 25° | $x \times 10^6$ −80° | $x \times 10^6$ −190° |
|---|---|---|---|
| 4.0 | 0.5 (±0.05) | 0.9 | 2.4 |
| 7.2 | 0.9 | 1.8 | 4.4 |
| 10.3 | 1.4 | 2.5 | 5.6 |
| 11.9 | 1.3 | 1.8 | 3.8 |
| 13.3 | 1.0 | 1.4 | 3.1 |
| 16.5 | 0.9 | 1.2 | 2.6 |
| 22.9 | 1.0 | 1.4 | 2.6 |
| 28.4 | 1.3 | 1.5 | 2.6 |
| 30.6 | 1.4 | 1.7 | 2.6 |
| 34.7 | 1.7 | 1.7 | 2.5 |

Reduction of the copper in the samples in all cases caused the magnetic susceptibility to drop substantially to zero. The susceptibility isotherms at −180° for oxidized, reduced and reoxidized copper–alumina are compared in Fig. 2.

The magnetic susceptibility of the sample prepared by multiple impregnation was $2.45 \times 10^{-6}$ at −170°. The susceptibility of the copper in this catalyst, which contained 5.2% copper, was, therefore, $51 \times 10^{-6}$ at −170°.

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[1] This is the third paper on the susceptibility isotherm from this Laboratory. The second paper appeared in THIS JOURNAL, **69**, 2698 (1947). Descriptions of magnetic, X-ray and surface area experimental methods will be found in the earlier papers.