

Figure 1.

quoted is Badger's rule¹ for stretching force constants

$$F = 1.86 \times 10^5 / (R_e - d_{ij})^3 \text{ dynes cm.}^{-1} \quad (1)$$

where R_e is the equilibrium bond length in Å, and d_{ij} is a function of the position of bonded atoms in the periodic table. Herschbach and Laurie² showed that an even simpler relation gave a better over-all correlation (excepting only diatomic alkali metal molecules)

$$R_e = a_{ij} - b_{ij} \log F \quad (2)$$

where a_{ij} and b_{ij} depend only on the rows of the periodic table of the two atoms being bonded, with the transition elements being regarded as a separate row.

The continuity of bonding between ordinary molecules and the loose, Lennard-Jones, noble gas, two-atom pair is given by extending eq. 2 to noble gas clusters. The Lennard-Jones potential-energy function is

$$V = 4\epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right] \quad (3)$$

Values of ϵ and σ are tabulated by Hirschfelder, Curtiss, and Bird.³ The minimum in this function is found where $dV/dR = 0$, and it is

$$R_e = 2^{1/6} \sigma \quad (4)$$

The force constant in Badger's rule is defined as the second derivative of the potential-energy function, evaluated at the minimum

$$F = (d^2V/dR^2)_e = 72\epsilon/2^{1/3}\sigma^2 \quad (5)$$

In terms of ϵ/k and σ as tabulated in ref. 3, p. 1110, the Lennard-Jones stretching force constant is

$$F = \frac{79.06(\epsilon/k)}{\sigma^2} \text{ dynes cm.}^{-1} \quad (6)$$

For homonuclear clusters, He-He, Ne-Ne, etc., the

"bond length" is found from eq. 4, and the "force constant" from eq. 6. For heteronuclear clusters, He-Ne, Ne-Ar, etc., the usual combination rules are used

$$\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2} \quad (7)$$

$$2\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})$$

The points for stable H_2 and all excited electronic states⁴ of H_2 are entered as Δ in Fig. 1, and the He-He cluster is similarly entered. One straight line labeled H-H connects all these points, in agreement with eq. 2. All uncharged (that is, omitting HF^+ , etc.) diatomic molecules between H and members of the first row (Li through F) in ref. 2 are entered as +, all bonds between H and these elements in polyatomic molecules as tabulated by Cottrell⁵ are also entered, and the He-Ne cluster is so entered. With the exception of one excited electronic state of LiH labeled b, all these points lie very close to the straight line, H-1, in Fig. 1. All stable and excited, uncharged, diatomic,² and polyatomic⁵ molecules between members of the first row of the periodic table (excluding Li_2 , however) and the cluster Ne-Ne are entered as \circ in Fig. 1. Except for the point labeled a, an excited electronic state of N_2 , all these points lie very close to the line 1-1. This extraordinary correlation includes the following: CO, N_2 , $C\equiv C$, $C=C$, $C-C$, $C\equiv N$, $C-N$, $C-F$, NO, $O=O$, BN, $O-O$, FF, $C-F$, LiF, BeO, NeNe; Fig. 1 shows some sense of continuity of bonding between these extreme cases. With the exception of N_2 all molecules between members of the second row of the periodic table as given by ref. 2 and 5 are entered as ∇ in Fig. 1; some examples are NaCl, AlCl, Si_2 , P_2 , SiS, MgCl, Cl_2 , and ArAr. With the exception of K_2 , points in the third row of the periodic table are related to KrKr with the symbol \oplus in Fig. 1. With the exception of Cs_2 , the members of the fourth row including XeXe are plotted

(1) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1933); **3**, 710 (1934).

(2) D. R. Herschbach and V. W. Laurie, *ibid.*, **35**, 458 (1961); Lawrence Radiation Laboratory Report 9694 (1961).

(3) J. O. Hirschfelder, C. F. Curtiss, and B. R. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954.

(4) G. Herzberg, "Spectra of Diatomic Molecules," D. van Nostrand Co., Inc., New York, N. Y., 1930, pp. 530-532.

(5) T. L. Cottrell, "The Strength of Chemical Bonds," 2nd Ed., Butterworths Scientific Publications, London, 1958.

TABLE I
PARAMETERS a_{ij} AND b_{ij} FROM EQ. 2 INCLUDING NOBLE GAS
CLUSTERS BUT OMITTING HOMONUCLEAR ALKALI METAL
MOLECULES

	H	1	2	3	4	3T	4T
a_{ij}							
H	1.18	1.46	1.74	1.82	1.96	1.71	1.81
1		1.85	2.06	2.15	2.28	2.12	2.22
2			2.36	2.45	2.62		
3				2.57	2.71		
4					2.87		
b_{ij}							
H	0.58	0.56	0.64	0.66	0.72	0.71	0.78
1		0.55	0.63	0.64	0.70	0.72	0.73
2			0.70	0.73	0.79		
3				0.74	0.81		
4					0.87		

as X in Fig. 1. In each case the noble gas cluster and the ordinary molecules lie close to a single straight line.

Similarly, all molecules from ref. 2 and 5 were plotted, such as H-2, 1-2, 2-3, 3-4, etc. The parameters a_{ij} and b_{ij} of eq. 2 for all cases are given in Table I. It can be seen that these terms vary slowly and smoothly over the periodic table. The constant b_{ij} is closely related to Pauling's constant 0.6, which defines bond order in terms of bond length.⁶ When b_{ij} is 0.6 (it almost always is close to this value) then the force constant is directly proportional to Pauling's bond order.

On very tenuous grounds, a similar correlation between dissociation energy and bond length was recently proposed.⁷ The present correlation between force constants and bond lengths is much more heavily documented and much more nearly convincing. This striking evidence for continuity of bonding for all types of bonds may be taken as support for the previous⁶ postulate, which interpolated bond energies between that for noble gas pairs and that for ordinary single-bonded molecules.⁵

(6) L. Pauling, *J. Am. Chem. Soc.*, **69**, 542 (1947).

(7) H. S. Johnston and C. Parr, *ibid.*, **85**, 2544 (1963).

(8) This research was supported by NSF Grant G-20976.

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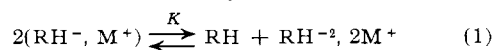
RECEIVED JANUARY 24, 1964

Electron Transfer Equilibria.

III. Disproportionation of Monoalkali Adducts of Stilbene¹

Sir:

The previously reported behavior of the monoalkali adducts of stilbene suggests that they show little tendency to disproportionate (eq. 1).²⁻⁴ We have found that by proper choice of solvent and metal ion the range of K can be made to vary from $<10^{-3}$ to $>10^3$.



As in the case of the alkali metal adducts of tetraphenylethylene,^{1,5} the disproportionation constant is a

(1) (a) Part I: J. F. Garst and R. S. Cole, *J. Am. Chem. Soc.*, **84**, 4352 (1962); (b) part II: J. F. Garst, E. R. Zabolotny, and R. S. Cole, *ibid.*, in press.

(2) D. E. Paul, D. Lipkin, and S. I. Weissman, *ibid.*, **78**, 116 (1956).

(3) K. Morigaki, K. Kuwata, and K. Hirota, *Bull. Chem. Soc. Japan*, **33**, 958 (1960).

(4) J. W. B. Reesor, J. G. Smith, and G. F. Wright, *J. Org. Chem.*, **19**, 940 (1954).

TABLE I

DISPROPORTIONATION CONSTANTS OF MONOALKALI STILBENES

Metal	Diethyl ether	Dioxane	2-MeTHF	THF
Li	$>10^3$	NR ^a	$>10^3$	$<10^{-3}$
Na	NR ^c	20	0.1	$<10^{-3c}$
K	NR	NR	Small ^b	Small ^b

^a No reaction could be visually detected. The surface of the metal was not discolored. ^b Dilute solutions only could be formed. The spectra appeared to be that of the monoalkali adduct only. ^c A disproportionation constant near 1 could be obtained in an ether-rich solvent mixture of diethyl ether and tetrahydrofuran.

sensitive function of the solvent and metal ion employed. However, a metal ion effect in the opposite direction from that observed with tetraphenylethylene is noted, increasing cationic radius leading to smaller, rather than larger, values of K . These results are detailed in Table I.

Three important conclusions are suggested by these observations: (1) Although there is a distinct quantitative difference between K for tetraphenylethylene and that for stilbene, under comparable conditions, it now appears that the same *kind* of disproportionation behavior for both and that the same kinds of structural and environmental factors influence K in each case. The pronounced influence of variation of solvent and metal ion, among ethers and alkali metals, is again emphasized by the stilbene data, suggesting that an observed value of K depends on a rather delicate balancing of ionic aggregation and solvation effects to which K is very sensitive.

(2) For a substituted olefin, the presence of steric strain in the hydrocarbon (present in tetraphenylethylene, absent in stilbene) is *not* a necessary condition for disproportionation of a monoalkali adduct to a directly measurable extent. It is quite possible, however, that the quantitative difference between the disproportionation behavior of stilbene and tetraphenylethylene is a reflection of a change in the geometries of the carbon skeletons of the dialkali adducts, relative to the monoalkali adducts and hydrocarbons.⁶ The disproportionation of monoalkali tetraphenylethylenes, but not monoalkali stilbenes, might then be accompanied by relief of steric strain,⁷ accounting for the relative magnitudes of K .

(3) If the same kinds of metal ion effects are to be invoked in both the stilbene and tetraphenylethylene cases, the observation of opposing directions of metal ion effects requires the operation of at least two opposing effects. One likely possibility considers the effects of ionic aggregation (considered as if in the gas phase) and those of ion and/or ion aggregate solvation as a pair of such opposing effects. In the gas phase, association of the metal ions with RH^- and RH^{-2} to give ion pairs and triple ions, respectively, should favor (coulombically) larger values of K , smaller cationic radii leading to larger values of K than larger cationic radii. On the other hand, ion pairs should be more

(5) A. G. Evans and B. J. Tabner, *J. Chem. Soc.*, 4613 (1963).

(6) (a) D. W. Ovenall and D. H. Whiffen, *Chemical Society Special Publication No. 12*, 1958, p. 139; (b) discussion of M. J. S. Dewar, *ibid.*, p. 164; (c) discussion of N. S. Hush, *ibid.*, p. 164; (d) discussion of P. Gray, *ibid.*, p. 166.

(7) The situation would then resemble that proposed for the alkali adducts of cyclooctatetraene, for which K is large, except that the roles of hydrocarbons and the dialkali adducts, insofar as strain is concerned, would be interchanged.⁸

(8) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784 (1960).