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A COMPARISON OF VALENCE SHELL AND CORE
IONIZATION POTENTIALS OF ALKYL IODIDES

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and A. Streitwieser, Jr.

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A Comparison of Valence Shell and Core Ionization Potentials of Alkyl Iodides.¹

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Sir:

It has recently been shown that the n, valence shell lone pair ionization potentials of alkyl iodides, bromides, and chlorides correlate well with Taft's σ^* values (as used with the Hammett equation)² and even better with each other.³

(2) R. W. Taft, "Steric Effects in Organic Chemistry," ed. by M. S. Newman, John Wiley, New York (1956) ch. 13.

(3) F. Brogli, J. A. Hashmall, and E. Heilbronner, Helv. Chim. Acta, work in the process of publication.

Similar correlations have been found between the iodide ionization potentials and those of a series of other alkyl substituted groups.⁴ We wish to report the

(4) B. J. Cocksey, J. H. D. Eland, and C. J. Danby, J. Chem. Soc., (B), 790 (1971).

$3d_{5/2}$ ionization potentials of a series of alkyl iodides and, by comparison with the valence shell ionization potentials, to elucidate the probable cause of the

chemical shifts and the magnitude of hyperconjugation in these compounds.

Table I contains the iodine $5p_{1/2}$ ionization potentials³ of a series of alkyl halides. Also shown are the shifts in ionization potential of the iodine $3d_{5/2}$ level relative to trifluoromethyl iodide. These latter values were obtained using an x-ray photoelectron spectrometer which has been described previously.⁵ A mixture of the sample and reference gases was introduced into

(5) C. S. Fadley, S. B. M. Hagstrom, M. D. Klein, and D. A. Shirley, J. Chem. Phys., 48 (8), 3779 (1968).

the target chamber and irradiated with Mg K α x-rays. The spectra of the mixtures were well-resolved, and the relative position of the sample peak was determined in each case by a least-squares fit of the two peaks with Gaussian functions. The observed spectra of the cases with greatest and least shifts relative to trifluoromethyl iodide (tert-butyl iodide and methyl iodide, respectively) are shown in fig. 1. In the case of hydrogen iodide, isopropyl iodide was used as a reference, but the tabulated shift is given relative to trifluoromethyl iodide.

The iodine $5p_{1/2}$ ionization potentials are plotted against the corresponding $3d_{5/2}$ chemical shifts in fig. 2. The least-squares straight line fit of these points, excluding the HI point, is also shown in this figure. The ionization potentials of the 3d orbitals show a wider range of variation than do those of the 5p orbitals (i.e. the slope is greater than 1), and the point for hydrogen iodide falls off the line despite the fact that the hydrogen halides fit the corresponding interhalogen correlations given in ref. 3.

The first observation suggests that the chemical shifts among the alkyl iodides arise from local variation in electronic charge distribution near the

TABLE I. Summary of the Iodine $5p_{1/2}$ Binding Energies and Relative $3d_{5/2}$ Binding Energies for Compounds of the Form R-I.

R	$5p_{1/2}$ Binding Energy ^a (eV)	$3d_{5/2}$ Chemical Shift ^b (eV)
-methyl	10.14	1.10 ± 0.03
-ethyl	9.93	1.36 ± 0.03
n-propyl	9.83	1.45 ± 0.04
n-butyl	9.81	1.49 ± 0.04
n-pentyl	9.78	1.51 ± 0.03
i-propyl	9.75	1.57 ± 0.03
t-butyl	9.64	1.73 ± 0.05
hydrogen	11.05	0.20 ± 0.04

(a) All errors ± 0.02 eV.

(b) Relative to trifluoromethyl iodide.

iodine atom, probably in the carbon-iodine bond; rather than from long-range charge-distribution effects (which would give a slope of unity in fig. 2). A through-bond (inductive) effect can be viewed as a shift of the electrons along the axis of the R-I bond. The electrons in this bond are, on the average, closer to core atomic orbitals than to the valence shell non-bonding p atomic orbitals, and consequently affect them more. This geometrical relation is illustrated in fig. 3.

An attractive explanation for the second observation is based on hyperconjugation--interaction with σ orbitals on the alkyl group is expected to destabilize electrons in the 5p levels as it stabilizes the σ electrons. This should have no effect on the core 3d levels. Hydrogen iodide cannot have such hyperconjugative destabilization. The displacement of this point from the line in fig. 2 indicates an average value of 0.14 eV for the hyperconjugative destabilization of I $5p_{1/2}$ electrons by alkyl groups. This relatively small effect is similar in magnitude to values calculated by Brogli and Heilbronner⁶

(6) F. Brogli and E. Heilbronner, Helv. Chim. Acta, in press.

using perturbation theory.

The present example demonstrates the unique advantages of using both valence shell and core photoelectron spectroscopy to elucidate the causes for chemical shifts of ionization potentials. We are continuing our studies of ionization potentials using these complementary techniques.

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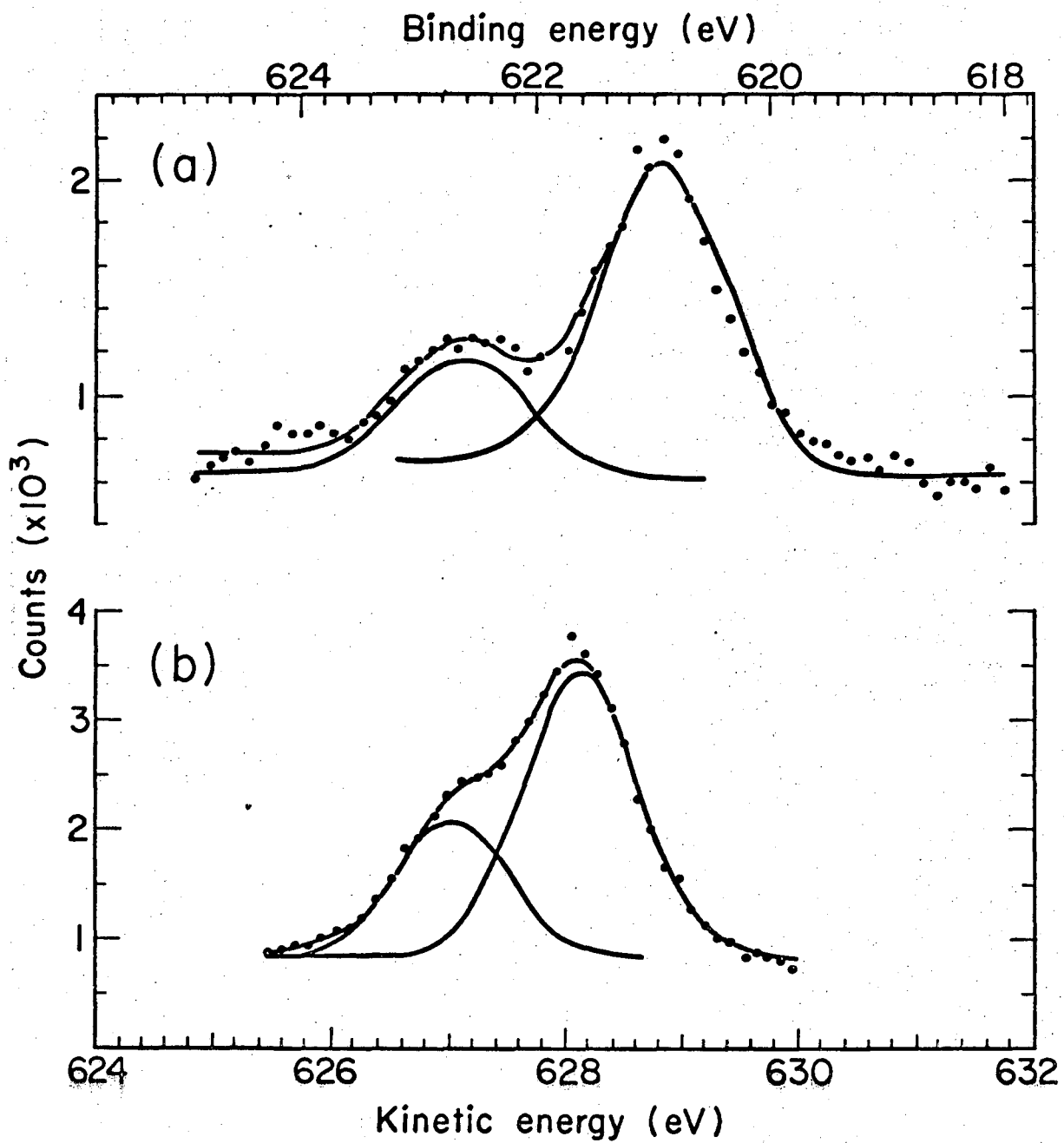
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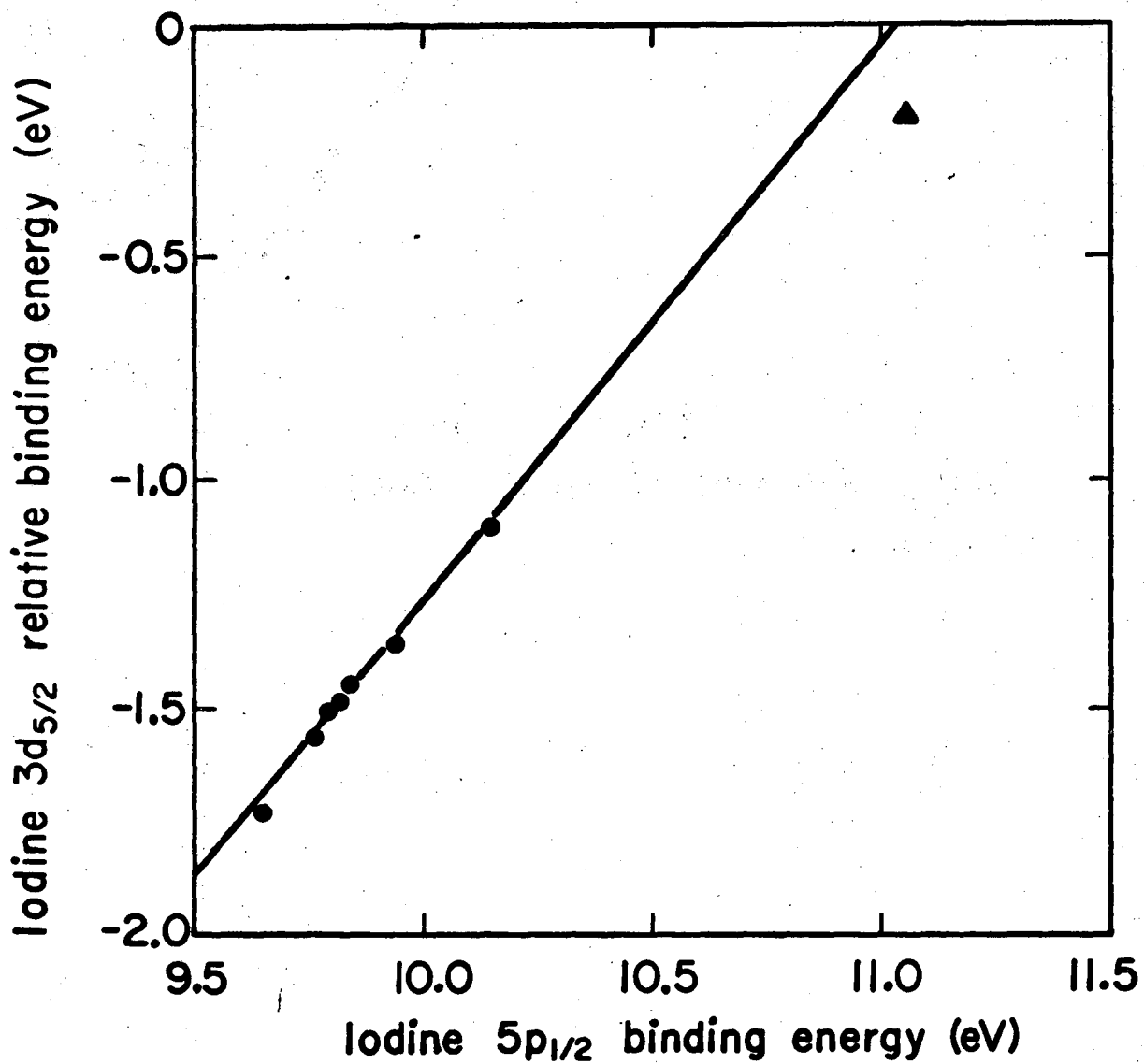
FIGURE CAPTIONS

- Fig. 1. Resolved photoelectron spectra of iodine $3d_{5/2}$ electrons from trifluoromethyl iodide with (a) tert-butyl iodide and (b) methyl iodide. Radiation was Mg $K\alpha$ x-rays.
- Fig. 2. Relative iodine $3d_{5/2}$ binding energy vs. iodine $5p_{1/2}$ binding energy, and least-squares straight line fit of all points except that for HI (Δ).
- Fig. 3. Diagram of the C-I bond length in relation to the average position of the 5p and 3d electrons. Note that r_{p-p} , the distance between the center of the C-I bond and the expected position of the 5p electron, is considerably longer than r_{p-d} .



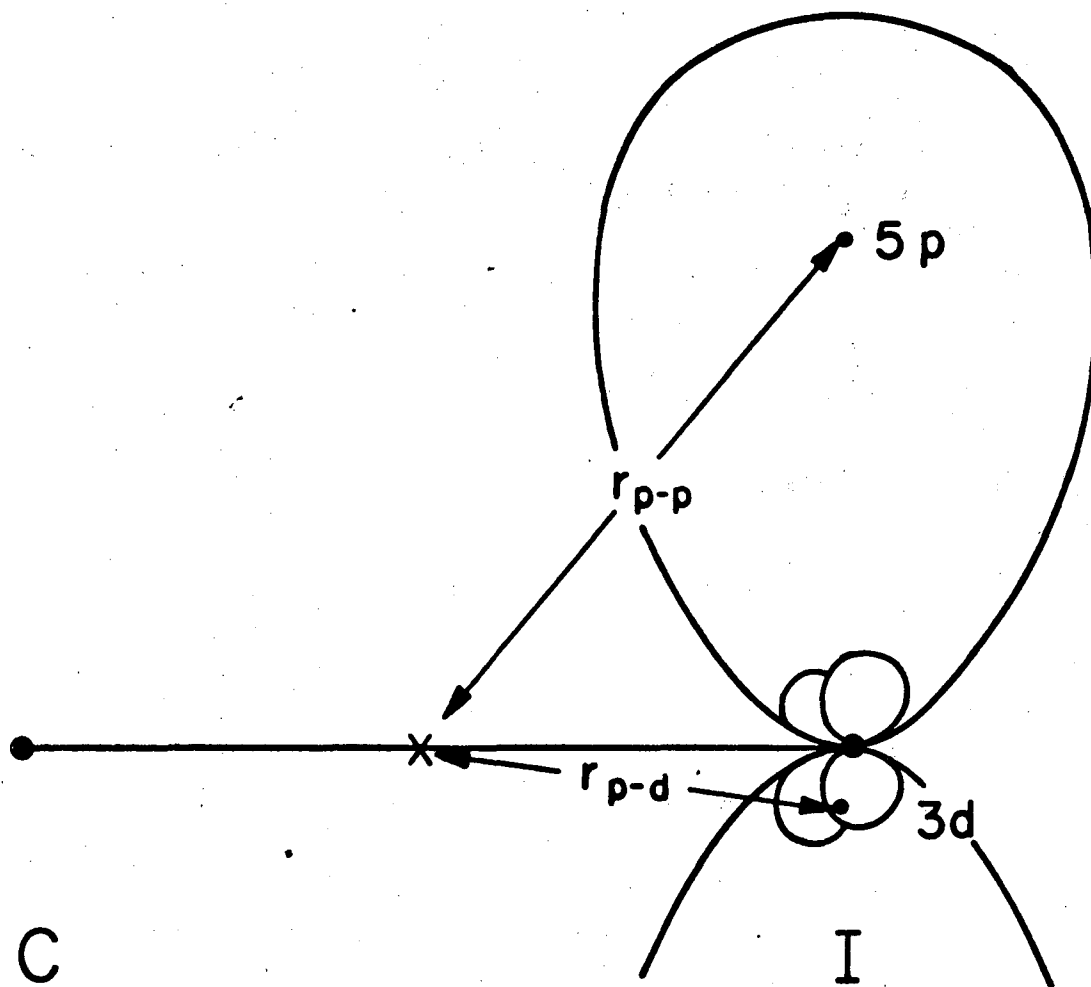
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Fig. 1



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Fig. 2



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Fig. 3

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