Secondary Processes. Reactions 0–11 lead to the following expressions for the quantum yields of CF_3H and H_2.

$$\Phi(CF_3H) = [k_1 + kk_7[Im]/(k_7 + k_8)]/(k_1 + k_2[Im]) \quad (15)$$

$$\Phi(H_2) = kk_9[Im]/(k_9 + k_{10})(k_1 + k_2[Im]) \quad (16)$$

That these expressions are of the correct form is apparent by taking the limiting values of [Im]. Then $\Phi^0(CF_3H) = 1$, $\Phi^\infty(CF_3H) = kk_7/k_2(k_7 + k_8)$, $\Phi^0(H_2) = 0$, and $\Phi^\infty(H_2) = kk_9/k_2(k_9 + k_{10})$. These limiting values predict that as [Im] increases, (CF_3H) will decrease in a parallel fashion to $\Phi(CF_3CN)$ but with a smaller limiting value. $\Phi(H_2)$ on the other hand will increase to its limiting value.

The limiting values of $\Phi(H_2)$ and $\Phi(CF_3H)$ can be estimated from Figures 2–5 and combined with k/k_2 to give approximate addition/abstraction ratios. We obtain $k_8/k_7 \simeq 70$, 50, and 20 at 100, 200, and 300°, respectively. These values may be compared with more accurate data recently obtained by Pritchard, *et al.*,[13] who photolyzed hexafluoroacetone in the presence of the imine. Their data yield $k_8/k_7 = 73$, 61, and 55 at the above temperatures and the agreement is most satisfactory. The rapid addition of CF_3 to imine results in the steady-state value of [CF_3] being reduced to the point where no C_2F_6 could be detected in our products.

Similar treatment of $\Phi^\infty(H_2)$ gives $k_{10}/k_9 \simeq 0.2$, 0.4, 2, and 20 at 25, 100, 200, and 300°, respectively. Thus H atoms appear to abstract more readily than they add to the imine at the lower temperatures.

In conclusion, eq 12, 15, and 16 give a satisfactory account of the behavior of $\Phi(CF_3CN)$, $\Phi(CF_3H)$, and $\Phi(H_2)$ as [Im] changes. The independence of these functions of intensity shown in Figure 6 is also justified.

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(13) D. W. Follmer, S. Toby, and G. O. Pritchard, *J. Phys. Chem.*, **76**, 487 (1972).

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

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Abstract: X-Ray photoelectron spectroscopy was used to study the relative ionization potentials of the iodine $3d_{5/2}$ level in a series of alkyl iodides and HI. Comparison of these data with the corresponding iodine $5p_{1/2}$ ionization potentials obtained from uv photoelectron spectroscopy establishes that the chemical shifts are probably due to variations in the electron distribution along the carbon–iodine bond and that the $5p_{1/2}$ level is destabilized about 0.14 eV by hyperconjugation.

It has recently been shown that the valence shell *n* 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] Similar correlations have been found between the iodide ionization potentials and those of a series of other alkyl-substituted groups.[4] We now report the $3d_{5/2}$ ionization potentials of a series of alkyl iodides. These results are compared with the valence shell ionization potentials to elucidate the probable cause of the chemical shifts and the magnitude of hyperconjugation in these compounds.

Experimental Section

The alkyl iodides are commercially available and were used without further purification.

The $3d_{5/2}$ binding energies were obtained using an X-ray photoelectron spectrometer which has previously been described in detail.[5] A mixture of the sample and the trifluoromethyl iodide used as the reference was introduced into the target chamber and irradiated with Mg Kα X-rays. The resulting 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 Figure 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 $3d_{5/2}$ peak was characterized in the usual way by its spin–orbit splitting behavior; it was chosen as a representative core level simply because it gives a relatively intense and easily characterized spectrum. The resulting $3d_{5/2}$ binding energies are summarized in Table I as chemical shifts relative to trifluoromethyl iodide. Table I also includes a summary of the iodine lone pair $5p_{1/2}$ ionization potentials from ref 3.

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(1) This research was supported in part by Grant No. 13369 of the National Science Foundation. Part of this work was performed under the auspices of the U. S. Atomic Energy Commission Contract No. W-7405-eng-48.

(2) R. W. Taft, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13.

(3) F. Brogli, J. A. Hashmall, and E. Heilbronner, *Helv. Chim. Acta*, in press.

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

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

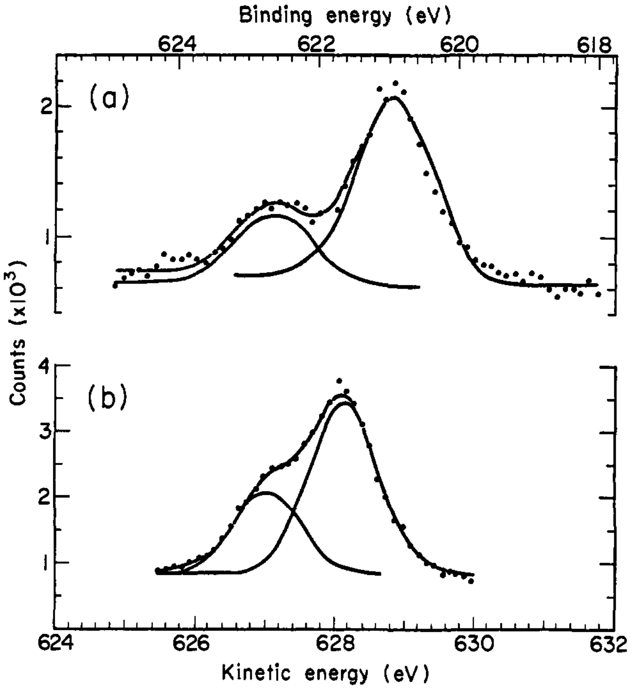

Figure 1. Resolved photoelectron spectra of iodine $3d_{5/2}$ electrons from trifluoromethyl iodide with (a) *tert*-butyl iodide and (b) methyl iodide. Radiation was Mg Kα X-rays.

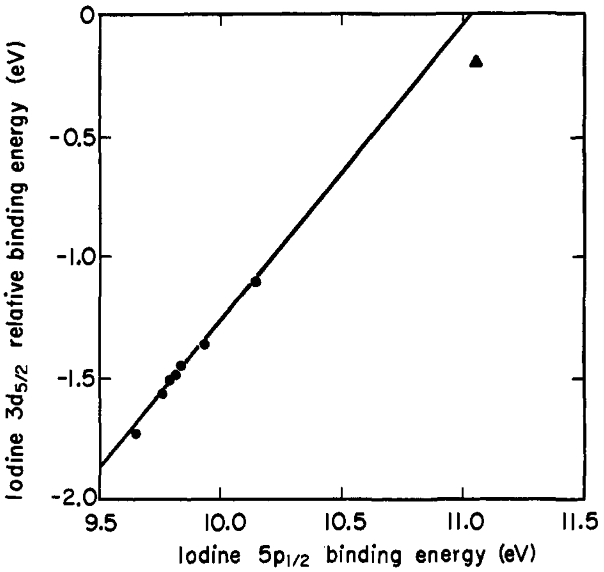

Figure 2. Relative iodine $3d_{5/2}$ binding energy *vs.* iodine $5p_{1/2}$ binding energy and least-squares straight line fit (slope = 1.22 ± 0.05) of all points except that for HI (▲).

Results and Discussion

A plot of the iodine $5p_{1/2}$ ionization potentials against the corresponding $3d_{5/2}$ chemical shifts is shown in Figure 2. The linear correlation for the alkyl iodide results contains two significant features that demand explanation. The least-squares line shown in Figure 2 has a slope, 1.22 ± 0.05, that is *greater* than unity and the point for hydrogen iodide falls off the line. The latter feature is significant because the hydrogen halides fit the corresponding interhalogen correlations given in ref 3.

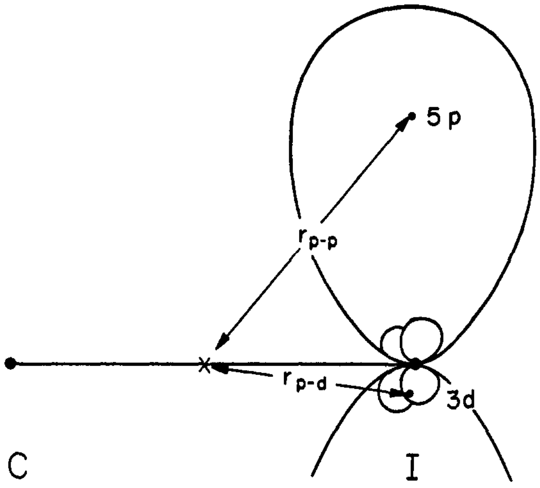

Figure 3. Diagram of the C–I bond length in relation to the average position of the 5p and 3d electrons. Note that r_{p-p}, the distance between the center of the C–I bond and the expected position of the 5p electron, is considerably longer than r_{p-d}.

Ionization potentials of various types are known to be responsive toward various measures of substituent behavior or inductive effects. What is surprising, at least at first sight, is that the valence shell lone-pair $5p_{1/2}$ ionization potential of iodine is *less responsive* to substituent change than is the core $3d_{5/2}$ ionization potential as given by the slope in Figure 2. We rationalize this result in the following way. 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 nonbonding p atomic orbitals and consequently affect them more. This geometrical relation is illustrated in Figure 3.

Table I. Summary of the Iodine $5p_{1/2}$ Binding Energies and Relative $3d_{5/2}$ Binding Energies for Alkyl Iodides

R in RI	$5p_{1/2}$ 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
Isopropyl	9.75	1.57 ± 0.03
tert-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.

This qualitative approach can be cast into more conventional MO language. The R–I bond can be written as a two-center MO made up of an approximately sp^3 hybrid orbital on carbon, ϕ_C, and a predominantly $5p_z$ orbital of iodine, ϕ_I, as in eq 1. The incorporation

$$\psi_{R-I} = a\phi_C + b\phi_I \qquad (1)$$

of some contribution from other iodine orbitals will not affect the argument to follow. A substituent on carbon will alter the coefficients, a and b, and the repulsion terms with other iodine electrons. From the relative distances involved, repulsion of other iodine electrons to the iodine fracton, b^2, of the R–I bond electrons will be more important than that with the carbon fraction, a^2. However, electron repulsion between electrons in different 5p orbitals is less than that between 5p and any core orbital. For example, in Hartree–Fock calculations on the iodine atom, the Coulomb repulsion integral $(5p_x5p_x/5p_z5p_z) = 0.69$ rydberg whereas that for $(3d_i3d_i/5p_z5p_z) = 0.99$ rydberg.[6]

The displacement of the point for hydrogen iodide from the alkyl iodide correlation line is plausibly explained by hyperconjugation. The iodine 5p levels are destabilized by interaction with appropriate σ orbitals on the alkyl group (hyperconjugation). This destabilization is partially offset by a stabilizing interaction with the corresponding σ^* orbitals (anionic hyperconjugation or backbonding). The core 3d levels are not affected by such interactions and provide a calibration for assessing the magnitude of the hyperconjugation effect; that is, the effect of structural change on the ionization potentials is dissected into an inductive and a conjugative effect. Only the former affects the core levels, whereas both contribute to the lone-pair 5p levels. Hydrogen iodide, on the other hand, cannot contain hyperconjugative interactions. The displacement of this point from the line in Figure 2 thus indicates an average value of 0.14 eV for the hyperconjugative destabilization of iodine $5p_{1/2}$ electrons by alkyl groups. This relatively small effect is similar in magnitude to values calculated by Brogli and Heilbronner[7] using perturbation theory. There is the further implication in the fit of all of the alkyl iodides to a single line that the hyperconjugative interaction with C–C bonds must be approximately the same as with C–H bonds.

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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(6) These numbers were calculated from the iodine atom results of J. B. Mann, "Atomic Structure Calculations I. Hartree–Fock Energy Results for the Elements Hydrogen to Lawrencium," LA-3690, TID-4500. The 3d–5p repulsions will depend, of course, on the specific d orbitals used but the differences are only in the third decimal. We thank Professor H. F. Schaefer III for helpful advice.

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

Stereochemical Course of a Gas-Phase Electrophilic Attack at Saturated Carbon. Reaction of *meso*-1,2-Dichloro-1,2-difluoroethane with Gaseous Brønsted Acids

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Abstract: The gas-phase electrophilic attack of He^3H^+ ions from the β decay of molecular tritium on *meso*-1,2-dichloro-1,2-difluoroethane leads to the predominant formation of a tritiated product *retaining the original configuration of the substrate*, with a considerably smaller yield of the tritiated *dl* form. The effect of the substrate pressure on the meso/*dl* ratio and the use of radiolytically produced methanonium and ethyl ions as milder gas-phase Brønsted acids show that the minor yield of the *dl* form is likely to arise from a racemization process, rather than from a discrete mode of attack, leading to inversion. The conclusion that the gas-phase tritiodeprotonation proceeds with retention of the substrate configuration is compared with the theoretical predictions on the course of the SE2 substitution processes.

The demonstration and the stereochemical study of a "pure" SE2 aliphatic substitution, *i.e.*, the electrophilic attack at saturated carbon with no additional interaction between the electrophile and the leaving group, represent one of the most interesting problems in the field of electrophilic reactions. In fact, in contrast with the wealth of information on the correspondent nucleophilic processes, the study of SE2 reactions has been almost exclusively restricted to metal ions as the leaving groups, and the results have been deeply influenced by the availability of vacant orbitals in the metal atoms, leading to the possibility of "bridging" between the electrophile and the leaving group.[1]

The results recently obtained in the study of the gas-phase reactivity of an exceedingly strong Brønsted acid, the helium tritide ion from the β decay of $^3H_2$,[2–6] suggested the possibility of investigating a gas-phase electrophilic process, characterized by a simple and well de-

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(1) For a comprehensive review, see F. R. Jensen and B. Rickborn, "Electrophilic Substitutions of Organomercurials," McGraw-Hill, New York, N. Y., 1968. Recently, however, examples of SE2 reactions involving the direct protonation of alkanes were reported by Olah and coworkers. See, *e.g.*, G. A. Olah, G. Klopman, and R. H. Schlosberg, *J. Amer. Chem. Soc.*, **91**, 3261 (1969).

(2) F. Cacace and S. Caronna, *ibid.*, **89**, 6848 (1967).

(3) F. Cacace, R. Cipollini, and G. Ciranni, *ibid.*, **90**, 1122 (1968).

(4) F. Cacace, M. Caroselli, R. Cipollini, and G. Ciranni, *ibid.*, **90**, 2222 (1968).

(5) F. Cacace, A. Guarino, and E. Possagno, *ibid.*, **91**, 3131 (1969).

(6) F. Cacace, A. Guarino, and M. Speranza, *ibid.*, **93**, 1088 (1971).