Variation in the *halide* species used in oxidation reactions proved to be the most intriguing parameter affecting product distributions (see Table I). Reactions between $Cp_2Zr(PPh_2Me)_2$ and 2-halobutanes illustrate this selectivity pattern: 2-iodobutane reacted rapidly to produce Cp_2Zr(*n*-butyl)I as the major product,[14] while the analogous chloride reacted more slowly to generate zirconocene dichloride as the predominant species. To elucidate this phenomenon, reactions between $Cp_2Zr(PPh_2Me)_2$ and *sec*-butyl chloride, bromide, and iodide were qualitatively followed by ^{1}H NMR. We note that reaction occurs immediately on mixing the zirconium species with each of these halides. For the iodide rapid growth of oxidative adduct is recorded; for the bromide, somewhat slower growth is observed; and, for the alkyl chloride, much slower growth is noted. Variation in formation rates for Cp_2ZrRX as a function of halogen atom *abstracted* is reminiscent of results reported for tin radicals[15] or for Cr(II) species.[16] These observations exclude significant participation of a recombination scheme such as the one shown in Scheme II: Here alkyl iodides would be expected to yield the *greatest* relative amount of Cp_2ZrX_2 and alkyl chlorides the least.

We conclude that whereas propagation depends dramatically on R·, L, and X, initiation is apparently not highly sensitive to variation in X.[17,18] It seems then that it is this discrepancy in discrimination profiles (iodides vs. bromides vs. chlorides) between these two competing routes, both of which involve attack of a metallic species upon an alkyl halide, which determines the overall outcome of these competitive oxidation processes.

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(18) Initiation may proceed by electron transfer in alkyl halide complexes of Zr(II). Electrochemical potentials for alkyl halides complexed to this or similar species have not been measured.

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Additions and Corrections

Statistical Phase Space Theory of Polyatomic Systems. Application to the Unimolecular Reactions $C_6H_5CN^{\cdot +} \rightarrow C_6H_4^{\cdot +} + HCN$ and $C_4H_6^{\cdot +} \rightarrow C_3H_3^{+} + {\cdot}CH_3$ [*J. Am. Chem. Soc.,* **99,** 1705 (1977)]. By WALTER J. CHESNAVICH and MICHAEL T. BOWERS,* Department of Chemistry, University of California, Santa Barbara, California 93106.

The right-hand side of eq 6 should be divided by σ_a. Also, eq 7 should read

$$R_{\mathcal{J}}(\mathrm{b}\rightarrow\mathrm{a}) = \frac{S_r'}{\sigma_b} \iint \bar{k}_{\mathcal{J}}(\mathcal{E}_r^{\,b},\mathcal{E}_t)\rho_t(\mathcal{E}_t)\rho_r(\mathcal{E}_r^{\,b}) \times \rho_b(E - \mathcal{E}_0 - \mathcal{E}_{tr}^{\,b})\, d\mathcal{E}_t d\mathcal{E}_{tr}^{\,b} \quad (7)$$

eq 8 should read

$$k_{\mathcal{J}}(E)_a = \frac{S_r'}{\sigma_b S_r \rho_a(E - \mathcal{E}_r^{\,a})} \iint \bar{k}_{\mathcal{J}}(\mathcal{E}_r^{\,b},\mathcal{E}_t)\rho_b(\mathcal{E}_t) \times \rho_r(\mathcal{E}_r^{\,b})\rho_b(E - \mathcal{E}_0 - \mathcal{E}_{tr}^{\,b})\, d\mathcal{E}_t d\mathcal{E}_{tr}^{\,b} \quad (8)$$

and equation (9a) should read

$$\bar{k}_{\mathcal{J}}(\mathcal{E}_r^{\,b},\mathcal{E}_t) = \mathcal{P}_b(\mathcal{E}_t,\mathcal{E}_r^{\,b},\mathcal{J})/2\pi\hbar\rho_t(\mathcal{E}_t)\rho_r(\mathcal{E}_r^{\,b}) \quad (9a)$$

where $\rho_r(\mathcal{E}_r^{\,b})$ is the density of rotational states of the separated fragments at rotational energy $\mathcal{E}_r^{\,b} = \mathcal{E}_{tr}^{\,b} - \mathcal{E}_t$. Equation 10a is correct as published.

In eq 10b–14, in the text surrounding these equations, and in Figures 2, 3, and 5, the quantity E should be replaced by E_v, the vibrational energy of the parent ion "a" except as follows; E should be replaced by $E_v + \mathcal{E}_r^{\,a}$ in the right-hand side of eq 10b, in both sides of eq 11 and 12, and in the first argument of $\mathcal{P}_{\mathcal{J}}$ in eq 14. These replacements are based on the standard assumption that the rotational angular momentum and rotational constant of the parent neutral are unaltered by the ionization process. Also the right-hand side of eq 10b should be divided by the rotational partition function of the parent molecule, and the right-hand side of eq 14 should be divided by a (numerically determined) normalization constant.

For clarification, S_r' always equals $2\mathcal{J}$, and $\mathcal{P}_b(\mathcal{E}_t,\mathcal{E}_r^{\,b},\mathcal{J})$, $\Gamma_b(\mathcal{E}_{tr},\mathcal{J})$, $\bar{k}_{\mathcal{J}}(\mathcal{E}_r^{\,b},\mathcal{E}_t)$, $k_{\mathcal{J}}(E)_a$, and $k_{\mathcal{J}}(E,\mathcal{E}_t)_a$ are functions of both $\mathcal{J}$ and its projection on a space-fixed axis. Furthermore, if the parent molecule is treated as a spherical top, then $k_{\mathcal{J}}(E)_a$ and $k_{\mathcal{J}}(E,\mathcal{E}_t)_a$ are also functions of the projection of $\mathcal{J}$ on a body-fixed axis and $g_{\mathcal{J}}$ in eq 10b equals $(2\mathcal{J})^2$. Also, note that $\int \bar{k}_{\mathcal{J}}(\mathcal{E}_r^{\,b},\mathcal{E}_t)2\mathcal{J}_t\, d\mathcal{J} = k_L$, where k_L is the Langevin capture rate constant.

Finally, a minor error was found in our RRKM computer program which, when corrected, required minor changes (~10%) in the transition state frequencies in order to reproduce the RRKM curves plotted in Figures 3 and 5.

None of the errors or misprints affect in any way the general conclusions of this paper.

Catalytic Decarbonylation of Aldehydes [*J. Am. Chem. Soc.,* **100,** 7083 (1978)]. By D. H. DOUGHTY and L. H. PIGNO-