Table II. Heats of Formation of the Acylium Ions ($R{-}C^+{\equiv}O$) in the Gas Phase

R	ΔH_f, kcal/mol Exptl[a]	 Calcd[b]
Me	153	157
Et	143	145
i-Pr	133	133
tert-Bu		121

[a] Reference 11. [b] Calculated using the MINDO approximations.

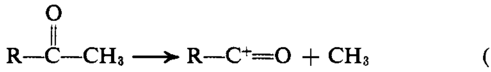
carried out. The results of these calculations are shown in column 2 of Table II. The C–O and C–C$^+$ bond lengths were taken from the literature[15] and the remaining C–C and C–H bond lengths are shown in Table III. All parameters for the one-electron resonance integrals were the same as given by Baird[14] except for $\beta_{CO}{}^{II}$, which was changed to 0.032 to adjust for the short C—O bond distance in $R{-}C^+{\equiv}O$.

Table III. Geometries Used in MINDO Calculations of Heats of Formation of the Oxocarbonium Ions

Bond	Length, Å	Bond	Angle, deg
C$^+$–O	1.108[a]	C–C$^+$–O	180
C–C$^+$	1.385[a]	$^+$C–C–H	108
C–H (α-C)	1.070	$^+$C–C–C	108
C–C	1.500		
C–H (methyl)	1.100 ± 0.005		

[a] Reference 15.

It would be nice to compare heats of formation of the ions in the gas and liquid phases, but the necessary thermochemical data on the acid chlorides are unavailable. The requisite measurements are currently underway here. However, the substituent effects on heats of reaction to give the cation in the gas phase and in solution are readily available. The gas-phase heats of formation from Table II can be combined with the gas-phase heats of formation of the methyl ketones and CH_3 to give the heats of reaction 2 in



$$\mathrm{R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_3 \longrightarrow R{-}C^+{\equiv}O + CH_3} \qquad (2)$$

the gas phase. These data are shown in Table IV. Since we are interested in substituent effects, the leaving-group effects will cancel in each series. Thus the heats of reaction in Tables I and IV show the effect of changing substituents on the difference in energy between the starting material and ionic product.

Table IV. Heats of Reaction 2 in the Gas Phase at 25°

R	ΔH_R, kcal/mol
Me	+238
Et	+234
i-Pr	+229
tert-Bu	+225[a]

[a] Calculated using the heat of formation of *tert*-Bu—C$^+$≡O given in Table II (MINDO) and the heats of formation of *tert*-butyl methyl ketone and CH_3 from ref 11. A slightly lower value (223 kcal/mol) is obtained if the heat of formation of methyl *tert*-butyl ketone reported by Cox and Pilcher is used: J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970, p 208.

The data in Tables I and IV permit a direct comparison between the substituent effect on a reaction in the gas phase and in solution.[16] The normal inductive order which is observed in the gas phase becomes a Baker–Nathan order in solution. This is a case where the Baker–Nathan order must be ascribed to solvent effects.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. Partial support by the National Science Foundation is also gratefully acknowledged.

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(13) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969).

(14) N. C. Baird, M. J. S. Dewar, and R. Sustmann, *ibid.*, **50**, 1275 (1969).

(15) F. P. Boer, *J. Amer. Chem. Soc.*, **90**, 6706 (1968).

(16) For the most recent in a long series of papers reporting investigations of the difference in the substituent effect of simple alkyl groups in the gas phase and in solution, see ref 5. Schubert's work contains several examples of substituent effects on electronic transitions which are reversed on passage from the gas phase to a solvent.

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Appropriate Nonbonding Orbitals for Describing Photophysical Properties in Benzaldehyde[1]

Sir:

Early valence views conceived of a lone-pair electron density highly concentrated at the carbonyl oxygen.[2] More recently a number of all-valence-electron calculations yielded very substantial delocalization of all valence orbitals in the ground state.[3] Admittedly, these calculations are as yet inexact; nevertheless, no support to the localized or delocalized view can be given by MO theory because the distinction between "localized" and "nonlocalized" orbitals is not an unambiguous one. It is possible to localize or delocalize an orbital at will by suitable unitary transformations among the occupied orbitals with no change in the total wave function for a given state. Any ground-state observable must then be predicted equally well by localized or delocalized orbitals.

In describing an excited state, a construct primarily used is the virtual-orbital model.[4] In this model, the excited-state wave function (Ψ_s) is obtained from the ground state (Ψ_0) by replacing one (or more) of the ground-state orbitals by virtual orbitals. An important feature of this construct is that orbitals common to both states are not reorganized. Not all unitary transformations on the occupied ground-state orbitals will leave such an excited-state wave function unaffected, so that observables computed with the excited-state wave function will in general be dependent on the transformation.

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(1) (a) Supported by National Science Foundation Grant No. GP 6301X; (b) presented at the EUCHEM Conference on Photophysical Processes, Schloss Elmau, Germany, Oct 25–31, 1970.

(2) R. S. Mulliken, *J. Chem. Phys.*, **3**, 564 (1935).

(3) *E.g.*, (a) J. M. Hollas, E. Gregorek, and L. Goodman, *ibid.*, **49**, 1745 (1968); (b) D. B. Neumann and J. W. Moskowitz, *ibid.*, **50**, 2216 (1969); (c) R. Hoffmann and J. R. Swenson, *J. Phys. Chem.*, **74**, 415 (1970); (d) E. Clementi, *J. Chem. Phys.*, **46**, 4737 (1967), for azines.

(4) *E.g.*, R. S. Mulliken, *J. Chim. Phys.*, *Physicochim. Biol.*, **46**, 497 (1949); C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

We restrict ourselves to the probability, P, of some photophysical process defined by an operator $\mathcal{O}$ in going from the ground state to the excited state. This is $P \propto \langle\Psi_0|\mathcal{O}|\Psi_s^*\rangle\langle\Psi_0^*|\mathcal{O}|\Psi_s\rangle$. Considering the case of single-electron operators and promotion from orbital ϕ_i to the virtual ϕ_j, it follows that $P \propto \langle\phi_i|\alpha|\cdot\phi_j\rangle^2$, since Ψ_0 and Ψ_s are single configurational wave functions. An important point in the present context is that $\mathcal{O}$ sorts out ϕ_i and ϕ_j from the orbital manifold. The probability is then controlled by the regionalization of the transition density $\phi_i\phi_j$ relative to $\mathcal{O}$.

As an example, the electric dipole radiative probability of a strongly allowed electronic transition is given by

$$P \propto e^2\langle\phi_i|\mathbf{r}|\phi_j\rangle^2 = \mathbf{M}_{ij}\cdot\mathbf{M}_{ij} \qquad (1)$$

Since $\mathbf{r}$ spans the entire molecule the dependence of the electric dipole radiative probability on the regionalization of $\phi_i\phi_j$ is not in general very marked.

It is emphasized that it is the construct that causes P to depend on the regionalization of $\phi_i\phi_j$. Because chemists think in terms of orbitals, the predictions made and the experiments designed will tend to a large extent to depend on the description of ϕ_i and ϕ_j. An appropriate question within the virtual-orbital model then concerns which orbitals are most appropriate to describe photophysical processes.

As noted above, $\mathbf{r}$ is not particularly regionalized so that the probability of a highly allowed transition does not allow $\phi_i\phi_j$ to be regionally probed. We therefore turn to the strength of the various single-quantum *nontotally symmetric* vibronic bands in a forbidden electronic band spectrum. For the electronic transition $\Psi_s \leftarrow \Psi_0$ (corresponding to the orbital promotion $\phi_j \leftarrow \phi_i$) the strength of the νth vibrational mode ($f_{00,s\nu}$) is approximated by[5]

$$f_{00,s\nu} \propto \sum_a\left(\frac{\partial\mathbf{M}_{ij}(Q_a)}{\partial Q_a}\right)^2_{Q_a=0}\langle\chi_{00}|Q_a|\chi_{s\nu}\rangle^2 + \ldots \qquad (2)$$

The molecule is considered cold, so that only the zero-point vibrational level of the ground state is populated. Q_a represents the ath normal coordinate in the ground state, enabling the molecule to be promoted to the νth vibrational mode in the excited state. The electric-dipole matrix element for the $\phi_j \leftarrow \phi_i$ promotion in the vibrationally distorted molecule is $\mathbf{M}_{00,s\nu}(Q_a) = e\langle\phi_i(Q_a)|\mathbf{r}|\phi_j(Q_a)\rangle$. For a forbidden transition $\mathbf{M}_{ij}$ vanishes at the equilibrium conformation of the ground state ($Q_a = 0$).

The set of normal coordinates Q_a is more or less regionalized. For example, in benzaldehyde, one normal coordinate describes primarily the aldehyde-hydrogen wag, others describe various skeletal motions of the ring, and so on. If, for example, the appropriate n orbital density to describe the $\pi^* \leftarrow$ n transition probability vanishes or is very low in the ring, an active nontotally symmetric ring vibration is not expected to appear in the $\pi^* \leftarrow$ n spectrum of benzaldehyde. Since $\mathbf{r}$ spans the entire molecule and π^* the entire skeletal part of the molecule, the delocalization of n is seen to be the significant factor.

Isotopic substitution provides a means whereby the extent of localization of $\phi_i\phi_j$ may be further probed. The effect of deuterium substitution on the out-of-plane vibrations (in the region 600–1000 cm^{-1}, where hydrogen motions dominate) is particularly marked. A detailed knowledge of the new normal coordinate coupled with the observed changes in the vibronic band strengths allows considerable information concerning the mapping of $\phi_i\phi_j$ to be obtained through eq 2.

A second example of a regionalized orbital sorting operator is provided by the spin–orbit coupling term appearing in the radiative probability between singlet and triplet states. The theory has been given in many places.[6] The transition moment $\mathbf{M}_{S_0\rightarrow T\sigma}$ between a singlet ground state (S_0) and the σth magnetic sublevel of a triplet state (T) generated by the orbital promotion $\phi_j \leftarrow \phi_k$ arising from a perturbing singlet (S_K)[7] generated by $\phi_j \rightarrow \phi_i$ is, to the first order

$$\mathbf{M}_{S_0\rightarrow T\sigma} = (E_{T\sigma} - E_{S_K})^{-1}\sum_\mu\langle\phi_k|H_{s0}{}^{\mu\sigma}|\phi_i\rangle\mathbf{M}_{ij} \qquad (3)$$

The spin–orbit coupling term at atom μ of proper symmetry to effect the σth sublevel is $H_{s0}{}^{\mu\sigma}$. If one atom has even moderately higher nuclear charge than the others, $H_{s0}{}^{\mu\sigma}$ is highly regionalized because of its Z^4 dependence. By varying the position of the principal spin–orbit coupling center in the molecule it is possible to map $\phi_k\phi_i$.

A combination of the two preceding examples, the probability of a nontotally symmetric vibration in the T → S_0 spectrum allows double-orbital sorting. The strength of such a vibronic band in the case of vibronic coupling between T_1 and T_2 and spin–orbit coupling between T_2 and S_K (S_K and T_1 generated by $\phi_j \leftarrow \phi_k$ and T_2 generated by $\phi_j \leftarrow \phi_i$) is, to the second order[8]

$$f^a{}_{S_0\rightarrow T_1} \propto \langle\phi_k|\sum_\mu H_{s0}{}^{\mu\sigma}|\phi_i\rangle^2\langle\phi_i|H_{ve}(Q_a)\phi_k\rangle^2(E_{S_K} - E_{T_1})^{-2}(E_{T_2} - E_{T_1})^{-2} \qquad (4)$$

where $H_{ve}(Q_a)$ is the perturbing Hamiltonian associated with the coupling vibration. Provided $H_{s0}{}^{\mu\sigma}$ and $H_{ve}(Q_a)$ are similarly regionalized, the strength of nontotally symmetric vibrations in $T_1 \leftarrow S_0$ will be stringently selected by the regionalization of $\phi_i\phi_k$.

In this communication, we address ourselves to whether the "nonbonding" orbital in benzaldehyde is best described as localized or delocalized (and how delocalized) for describing photophysical processes.

(1) The most active nontotally symmetric fundamental in the $\pi^* \leftarrow$ n system of benzaldehyde is an out-of-plane mode at 732 cm^{-1} involving the ring hydrogens.[3a,9] The aldehyde modes are much weaker. This observation is in accord with a nonbonding orbital delocalized into the ring.

(2) The 732-cm^{-1} band is assigned to ν_4 coupled to ν_{11}.[9–11] Since the calculated normal coordinate for this mode involves displacements of the hydrogens, deuteration at the para position should affect the intensity. In the deuterated compound, the only ob-

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[5] G. Herzberg and E. Teller, *Z. Phys. Chem., Abt. B*, **21**, 410 (1938).

[6] *E.g.*, L. Goodman and B. J. Laurenzi, *Advan. Quantum Chem.*, **4**, 153 (1968).

[7] The term arising from a perturbing triplet is dropped in eq 3 and 4 for simplicity. The reasoning herein does not lose its validity because of its omission.

[8] *E.g.*, R. M. Hochstrasser, "Molecular Aspects of Symmetry," W. A. Benjamin, New York, N. Y., 1966, Section 9.12.

[9] J. Smolarek, R. Zwarich, and L. Goodman, *J. Chem. Phys.*, in press.

[10] Notation of A. Langseth and R. C. Lord, *Kgl. Dan. Vidensk. Selsk. Mat.-Fys., Medd.*, **16**, No. 6 (1938).

[11] R. Zwarich, J. Smolarek, and L. Goodman, *J. Mol. Spectrosc.*, in press.

served out-of-plane hydrogen wagging modes correspond to bands at 711 and 816 cm^{-1}, both substantially weaker than the 732-cm^{-1} band in benzaldehyde itself. This observation requires the nonbonding orbital to have substantial density in the para region of the ring, if not at the para hydrogen atom itself.

(3) The lifetime ratio for the two-spin in-plane magnetic sublevels of the T(nπ^*) state is 0.4.[12] Equation 3 would predict this ratio to be $\ll 1$ for a localized orbital.

If photophysical processes in benzaldehyde are well described by a strongly delocalized n orbital as required by observations 1–3, then consideration of the vibronic spin–orbit coupling process described by eq 4 suggests an unusual process. Normally a weak $T_2(\pi\pi^*) \leftarrow S_0$ is not found coupled to the strong $T_1(n\pi^*) \leftarrow S_0$ because of the intrinsic weakness of $T_2 \leftarrow S_0$ (lifetimes for $\pi\pi^*$ states $\sim 10^{-1}$ sec, for nπ^* states $\sim 10^{-2}$–10^{-3} sec in carbonyl compounds). In benzaldehyde S_1 and T_1 are both generated by $\pi^* \leftarrow n$ and T_2 is described by $^3L_a(\pi\pi^*)$.[13] Since S_1 is the principal perturbing singlet,[13] eq 4 gives $f^a{}_{S_0 \rightarrow T_1} \propto \langle n|H_{s0}{}^{O\sigma}|\pi\rangle^2 \cdot \langle \pi|H_{ve}(Q_a)|n\rangle^2$, taking into account that oxygen is the atom with the highest nuclear charge. A strongly delocalized n orbital allows the vibronic factor to be sufficiently large for $T_2(\pi\pi^*) \leftarrow S_0$ to have an important vibronic interaction with the strong $T_1(n\pi^*) \leftarrow S_0$ in benzaldehyde. We have recently observed, in the $T_1(n\pi^*) \rightarrow S_0$ phosphorescence of benzaldehyde at 4.2°K (where sufficient resolution to sort out vibrations is obtained), active nontotally symmetric vibrations coupling T_1 to T_2.[13]

Our conclusions then are that substantially delocalized orbitals are more appropriate in describing photophysical processes in benzaldehyde than localized ones. Other areas where a delocalized model may also be fruitful are photochemistry and radiationless processes.

Acknowledgment. The authors thank Dr. Eugene A, Scarzafava for valuable discussions.

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[13] (a) R. Zwarich and L. Goodman, *ibid.*, 7, 609 (1970); (b) M. Koyangi and L. Goodman, *J. Chem. Phys.*, in press.

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Alkoxide-Induced Reactions of Tri-*n*-butylborane with Chlorodifluoromethane and Related Trisubstituted Methanes. A New, Facile Route from Organoboranes to the Corresponding Trialkylcarbinols

Sir:

Tri-*n*-butylcarbinol is obtained in essentially quantitative yield, 98%, from the rapid reaction of chlorodifluoromethane with tri-*n*-butylborane under the influence of lithium triethylcarboxide. Other trisubstituted methanes, such as chloroform, dichlorofluoromethane, and dichloromethoxymethane (1,1-dichlorodimethyl ether), also react readily, although in these cases the yields are somewhat lower, in the range of 80–85%. Consequently, this development provides an alternative to the carbon monoxide reaction as a route to the trialkycarbinols,[1-3] with the advantage of proceeding considerably more rapidly at lower temperatures.

$$n\text{-Bu}_3\text{B} + \text{CO} \xrightarrow[125°,\ 8\ \text{hr}]{\text{diglyme}} [\ ] \xrightarrow{[\text{O}]} \underset{90\%}{n\text{-Bu}_3\text{COH}} \qquad (1)$$

$$n\text{-Bu}_3\text{B} + \text{HCClF}_2 \xrightarrow[65°,\ 1\ \text{hr}]{\text{THF, LiOCEt}_3} [\ ] \xrightarrow{[\text{O}]} \underset{98\%}{n\text{-Bu}_3\text{COH}} \qquad (2)$$

The reaction of organoboranes with carbon monoxide provides a highly promising new route *via* hydroboration from olefins to tertiary alcohols.[3,4] However, for certain readily isomerized organoboranes it would be desirable to have an alternative reaction which would proceed readily at temperatures of 25–75°, a temperature range in which the isomerization of organoboranes is not significant.[5]

One approach that we considered was the preparation of trichloromethyllithium at low temperatures and its reaction with the organoborane. Indeed, the reaction of dichloromethyllithium with triarylboranes does provide a satisfactory route to the diarylcarbinols[6] (eq 3).

$$\text{Ar}_3\text{B} + \text{LiCHCl}_2 \xrightarrow{-74°} [\ ] \xrightarrow{[\text{O}]} \text{Ar}_2\text{CHOH} \qquad (3)$$

Accordingly, we prepared trichloromethyllithium from *n*-butyllithium and chloroform at −110°[7,8] and added tri-*n*-butylborane. The reaction mixture was allowed to come to room temperature. Oxidation of the intermediate with alkaline hydrogen peroxide provided a 37% yield of tri-*n*-butylcarbinol.

The instability of trichloromethyllithium[7] and the difficulties in preparing and utilizing it at very low temperatures on a preparative scale led us to search for a more convenient solution. We have recently realized considerable success in inducing the reaction of organoboranes with α-halo esters, ketones, and nitriles with alkoxide bases.[9] Accordingly, we decided to explore the possibility of inducing a reaction of chloroform and related trisubstituted methanes with a representative organoborane such as tri-*n*-butylborane with typical alkoxide bases.

Various alkoxides were examined. The results indicated that the more hindered alkoxides offered advantages, presumably because coordination with the organoborane was less complete. Thus in the reaction of chloroform with tri-*n*-butylborane potassium *tert*-butoxide provided a yield of 30% at both 0 and 65°. The yield improved with potassium triethylcarboxide, 50% at 0° and 59% at 65°. The reactions induced by the corresponding lithium bases were much slower, so that the higher temperature, 65° (refluxing THF), was adopted. Under these conditions lithium *tert*-butoxide gave a 55% yield in 1 hr, whereas lithium

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