Geometrical Effects in Molecular Orbital Calculations on Carbon-13 Coupling Constants in a Model Carbonium Ion[1]

Gary E. Maciel[2]

Contribution from the Department of Chemistry, University of California, Davis, California 95616. *Received November 24, 1970*

Abstract: The results of finite perturbation–INDO calculations of C–C, C–H, and C*CH* spin–spin coupling constants are presented for a variety of geometrical configurations of the isopropyl carbonium ion. The bond angles involving the central carbon were varied from the planar-trigonal value to the tetrahedral value. The effects on the computed couplings of altering the C–C bond lengths and the C–H bond length of the central carbon were explored. Calculations were carried out for several methyl-group conformations. The results are discussed in terms of approaches that are currently used in the interpretation of experimental data.

The structure of carbonium ions has been one of the main interests of organic chemists for several years. An immense body of largely circumstantial chemical evidence has been accumulated that has given rise to a variety of generalizations and patterns in the relationships between structure and reactivity.[3,4] Of the physical methods that have been applied in this area, probably the most productive has been nmr, extensive studies having been carried out by Olah and coworkers[5] and others.[6–12]

Many of the more recent nmr studies of carbonium ions employ ^{13}C magnetic resonance (cmr)[5–12] and show promise of providing important details on carbonium ion structures. The carbon-13 studies have essentially all been based upon the generation of positively charged species in very strong acid media. They have been directed to simple alkyl carbonium ions, as well as a variety of species generated from the action of strong acids upon oxygen-containing and nitrogen-containing functional groups.

Carbon-13 chemical shifts, short- and long-range C–H coupling constants, and even J_{CC} values have been reported for positively charged carbon species. Data on the cmr spectra of carbonium ions with reasonably well-defined structures have been employed as model cases for predictions of carbon chemical shifts and coupling constants that would correspond to structures proposed for species that have been only poorly understood. Such predictions have then been used, *via* comparison with actual experimental data, to choose the correct structure from among those that have been proposed. These predictions and choices were based largely on empirical relationships such as additivity rules[13] and/or the assumption that certain structural alterations leave ^{13}C parameters largely unchanged or changed by amounts that are empirically predictable from model cases. Such approaches have yielded especially interesting results in cases where chemical exchange leads to "averaged" values of chemical shifts and coupling constants and where, *a priori*, nonclassical ions may be involved. It was to provide a firmer basis for the use of model cases in such predictions that the current work was initiated.

In the ideal case, an MO theory would be capable of direct calculation of the nmr parameters of interest for any species or structure that is proposed as a possibility in accounting for experimental data. As a practical method, this direct approach is not yet available in many instances, so that empirical rules will continue to be useful. However, recently developed and emerging theories are capable of enhancing this usefulness by providing certain guidelines that are based upon the individual areas of strength of the theories. The approach employed in this work is the finite perturbation–INDO theory of spin–spin coupling developed by Pople, McIver, and Ostlund.[14] This theory has been applied previously to J_{CH} and J_{CC} calculations,[15] and the

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(1) Supported by National Science Foundation Grant No. GP 8119 and by Grant No. 3310-A4,5 from the Petroleum Research Fund, administered by the American Chemical Society.

(2) Address correspondence to the Department of Chemistry, Colorado State University, Fort Collins, Colo. 80521.

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Table I. The Effect of Changing the Angle α in the Isopropyl Cation[a,b]

α	$J_{C_1H_4}$	$P^2_{s_1s_4}$	$J_{C_1C_2}$	$P^2_{s_1s_2}$	$J_{C_2H_5}$	$P^2_{s_2s_5}$	$J_{C_2H_6}$	$P^2_{s_2s_6}$	$J_{C_2H_7}$	$P^2_{s_2s_7}$	$J_{C_2H_{567}}$[c]	$P^2_{s_2s_{567}}$[d]
120	146.55	0.2952	40.07	0.07145	125.49	0.2442	121.37	0.2455	121.37	0.2455	122.76	0.2451
118	149.84	0.2956	38.95	0.07017	125.45	0.2456	114.97	0.2373	128.82	0.2521	123.08	0.2450
116	153.83	0.2963	37.81	0.06885	125.55	0.2471	112.66	0.2335	132.14	0.2541	123.44	0.2449
114	158.67	0.2971	36.65	0.06755	125.78	0.2486	111.04	0.2304	134.77	0.2554	123.86	0.2448
112	164.54	0.2982	35.45	0.06625	126.13	0.2500	109.80	0.2278	137.07	0.2562	124.33	0.2447
110	171.73	0.2994	34.19	0.06487	126.58	0.2515	108.83	0.2254	139.18	0.2567	124.86	0.2445
Tetr[h]	173.89	0.2999	33.84	0.06452	126.71	0.2519	108.61	0.2249	139.72	0.2568	125.01	0.2445

[a] Coupling constants given in hertz; geometry notation given in Figure 1. [b] In all cases $R_{C_1C_2}$ = 1.52, $R_{C_1H_4}$ = 1.08, and the R_{CH} values within each methyl group are 1.09 Å. In each case the atoms H_4, C_1, C_2, and H_5 are in a plane and the atoms H_4, C_1, C_3, and H_8 are in a

Table II. Variation of the Bond Distances $R_{C_1C_2}$ and $R_{C_1H_4}$ in the Isopropyl Cation[a,b]

$R_{C_1C_2}$	$R_{C_1H_4}$	$J_{C_1H_4}$	$P^2_{s_1s_4}$	$J_{C_1C_2}$	$P^2_{s_1s_2}$	$J_{C_2H_5}$	$P^2_{s_2s_5}$	$J_{C_2H_6}$	$P^2_{s_2s_6}$	$J_{C_2H_{567}}$[c]
1.49	1.07	143.52	0.2923	39.60	0.07441	124.31	0.2414	120.15	0.2431	121.54
1.49	1.08	145.95	0.2906	39.61	0.07449	124.27	0.2414	120.18	0.2431	121.54
1.49	1.09	148.49	0.2890	39.62	0.07457	124.23	0.2413	120.20	0.2432	121.54
1.52	1.07	144.15	0.2968	40.07	0.07137	125.53	0.2442	121.35	0.2455	122.74
1.52	1.08	146.55	0.2952	40.07	0.07145	125.49	0.2442	121.37	0.2455	122.74
1.52	1.09	149.06	0.2935	40.07	0.07152	125.45	0.2441	121.39	0.2456	122.74
1.54	1.07	144.41	0.2996	40.46	0.06939	126.31	0.2461	122.14	0.2471	123.53
1.54	1.08	146.79	0.2979	40.46	0.06947	126.28	0.2460	122.16	0.2471	123.53
1.54	1.09	149.28	0.2962	40.46	0.06954	126.24	0.2460	122.18	0.2471	123.53

[a] Coupling constants given in hertz; geometry notation given in Figure 1. [b] In all cases the atoms C_1, C_2, C_3, H_4, H_5, and H_8 are in a plane. The R_{CH} values within each methyl group are 1.09 Å. [c] The average of $J_{C_2H_5}$, $J_{C_2H_6}$, and $J_{C_2H_7}$. [d] The average of $P^2_{s_2s_5}$, $P^2_{s_2s_6}$, and $P^2_{s_2s_7}$.

Table III. Variation of the Dihedral Angle $\Phi = \angle H_4C_1C_3H_8 = \angle H_4C_1C_2H_5$ in the Isopropyl Cation[a,b]

Φ	$J_{C_1H_4}$	$P^2_{s_1s_4}$	$J_{C_1C_2}$	$P^2_{s_1s_2}$	$J_{C_2H_5}$	$P^2_{s_2H_5}$	$J_{C_2H_6}$	$P^2_{s_2s_6}$	$J_{C_2H_7}$	$P^2_{s_2s_7}$	$J_{C_2H_{567}}$[c]	$P^2_{s_2s_{567}}$[d]
0	146.55	0.2952	40.07	0.07145	125.49	0.2442	121.37	0.2455	121.37	0.2455	122.74	0.2451
20	146.03	0.2946	40.23	0.07152	123.84	0.2435	118.83	0.2448	125.39	0.2469	122.69	0.2451
40	145.03	0.2937	40.57	0.07167	120.52	0.2425	117.72	0.2437	129.48	0.2487	122.57	0.2450
60	144.54	0.2932	40.74	0.07174	118.17	0.2426	118.17	0.2426	131.23	0.2496	122.52	0.2449
80	145.03	0.2937	40.57	0.07167	117.72	0.2437	120.52	0.2425	129.48	0.2487	122.57	0.2450
90	145.53	0.2941	40.40	0.07159	118.11	0.2443	122.21	0.2429	127.59	0.2478	122.64	0.2450
100	146.03	0.2946	40.23	0.07152	118.83	0.2448	123.84	0.2435	125.39	0.2469	122.69	0.2451
120	146.55	0.2952	40.07	0.07145	121.37	0.2455	125.49	0.2442	121.37	0.2455	122.74	0.2451

[a] Coupling constants given in hertz; geometry notation given in Figure 1. [b] In all cases the atoms C_1, C_2, C_3, and H_4 are in a plane. The R_{CH} values within each methyl group are 1.09 Å. $R_{C_1H_4}$ = 1.08 and $R_{C_1C_2}$ = 1.52 Å. [c] The average of $J_{C_2H_5}$, $J_{C_2H_6}$, and $J_{C_2H_7}$. [d] The average

major experimental patterns of structural dependence were accounted for. Except for some discrepancies, as the case of J_{CH} values for carbon to which $-I^-$ substituents are attached,[15a] this approach provided a level of agreement that had not been achieved by any other theory that is applicable to systems of experimental interest. While *absolute* agreement with experiment has been demonstrated to be only qualitative at best, the *trends* of calculated coupling constants with structural variations have been largely successful, especially as regards geometrical variations (*e.g.*, rotation about a C–C bond).[16] The present work is limited to such geometrical variations in order to maximize the validity and usefulness of the calculated results. Explored here are the effects of varying specific bond lengths and angles upon the computed J_{CH}, J_{CC}, and J_{CCH} values of a suitable model carbonium, arbitrarily chosen to be the isopropyl cation. The aim is to provide guidelines for the interpretation of relevant experimental data in which such geometrical variations may be suspected and/or under investigation.

Results

The spin–spin coupling constants between directly bonded carbons (J_{CC}), directly bonded carbons and hydrogens (J_{CH}), and geminally related carbons and hydrogens (J_{CCH}) were computed by previously reported methods,[14–16] according to

$$J_{AB} = h(4\beta/3)^2\gamma_A\gamma_B s_A{}^2(0)s_B{}^2(0)\left[\frac{\partial}{\partial h_B}\rho_{s_As_A}(h_B)\right]_{h_B=0} \qquad (1)$$

In this equation, h is Planck's constant, β is the Bohr magniton, γ_A is the magnetogyric ratio of nucleus A, $s_A{}^2(0)$ is the value of ϕ^2 at the nucleus A, where ϕ is the valence-shell s orbital centered on that nucleus, and $\rho_{s_As_A}(h_B)$ is the spin-density matrix element for ϕ_{s_A} that results in an unrestricted INDO[17] calculation from the presence of the Fermi contact perturbation (h_B) due to nucleus B. The "standard" geometry of the isopropyl cation upon which the structural variations were based is given in Figure 1. Table I gives the results obtained by varying the angle α, $\angle H_4C_1C_2 = \angle H_4C_1C_3 = \angle C_3C_1C_2$; this angle was varied from the 120° value that corresponds to trigonal C_1 to the tetrahedral value, while all other parameters are maintained constant and

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$J_{C_1H_5}$	$J_{C_1H_6}$	$J_{C_1H_7}$	$J_{C_1H_{567}}$[e]	$J_{C_2H_4}$[f]	q_{C_1}	q_{C_2}	q_{H_4}	q_{H_5}	q_{H_6}	q_{H_7}	$q_{H_{567}}$[g]
−7.618	−0.393	−0.393	−2.801	−1.762	3.6046	4.0342	0.9233	0.9346	0.8836	0.8836	0.9006
−5.512	−1.714	2.252	−1.658	−1.803	3.6067	4.0315	0.9219	0.9291	0.8724	0.9028	0.9014
−2.971	−1.122	2.723	−0.457	−1.806	3.6088	4.0288	0.9203	0.9240	0.8713	0.9113	0.9022
0.017	−0.092	2.505	0.810	−1.768	3.6110	4.0261	0.9185	0.9194	0.8720	0.9178	0.9031
3.479	1.193	1.780	2.158	−1.683	3.6132	4.0233	0.9165	0.9153	0.8735	0.9230	0.9039
7.464	2.663	0.618	3.582	−1.539	3.6156	4.0205	0.9142	0.9115	0.8757	0.9275	0.9049
8.614	3.077	0.241	3.972	−1.490	3.6163	4.0197	0.9135	0.9105	0.8763	0.9286	0.9051

plane. [c] The average of $J_{C_2H_5}$, $J_{C_2H_6}$, and $J_{C_2H_7}$. [d] The average of $P^2_{s_2s_5}$, $P^2_{s_2s_6}$, and $P^2_{s_2s_7}$. [e] The average of $J_{C_1H_5}$, $J_{C_1H_6}$, and $J_{C_1H_7}$. [f] The sum of the diagonal density matrix elements for atom C_1. [g] The average of q_{H_5}, q_{H_6}, and q_{H_7}. [h] The angle α has the tetrahedral value.

$P^2_{s_2s_{567}}$[d]	$J_{C_1H_5}$	$J_{C_1H_6}$	$J_{C_1H_{567}}$[e]	$J_{C_2H_4}$	q_{C_1}[f]	q_{C_2}	q_{H_4}	q_{H_5}	q_{H_6}	$q_{H_{567}}$[g]
0.2425	−7.782	−0.496	−2.925	−2.073	3.6024	4.0399	0.9283	0.9350	0.8799	0.8983
0.2425	−7.852	−0.530	−2.971	−2.112	3.6032	4.0397	0.9276	0.9350	0.8799	0.8983
0.2426	−7.926	−0.567	−3.020	−2.152	3.6040	4.0395	0.9270	0.9350	0.8800	0.8983
0.2451	−7.558	−0.363	−2.761	−1.731	3.6037	4.0344	0.9240	0.9346	0.8836	0.9006
0.2451	−7.618	−0.393	−2.801	−1.762	3.6046	4.0342	0.9233	0.9346	0.8836	0.9006
0.2451	−7.681	−0.425	−2.844	−1.795	3.6054	4.0341	0.9226	0.9347	0.8836	0.9006
0.2467	−7.429	−0.298	−2.675	−1.522	3.6048	4.0305	0.9213	0.9344	0.8860	0.9021
0.2467	−7.483	−0.326	−2.712	−1.549	3.6056	4.0303	0.9206	0.9345	0.8860	0.9022
0.2467	−7.539	−0.355	−2.750	−1.576	3.6065	4.0301	0.9198	0.9345	0.8861	0.9022

[e] The average of $J_{C_1H_5}$, $J_{C_1H_6}$, and $J_{C_1H_7}$. [f] The sum of the diagonal density matrix elements for atom C. [g] The average of q_{H_5}, q_{H_6}, and q_{H_7}.

$J_{C_1H_5}$	$J_{C_1H_6}$	$J_{C_1H_7}$	$J_{C_1H_{567}}$[e]	$J_{C_2H_4}$	q_{C_1}[f]	q_{C_2}	q_{H_4}	q_{H_5}	q_{H_6}	q_{H_7}	$q_{H_{567}}$[g]
−7.618	−0.393	−0.393	−2.801	−1.762	3.6046	4.0342	0.9233	0.9346	0.8836	0.8836	0.9006
−6.426	1.596	−3.516	−2.782	−1.857	3.6059	4.0333	0.9246	0.9259	0.8655	0.9100	0.9005
−3.645	1.367	−5.961	−2.746	−2.049	3.6087	4.0314	0.9272	0.9043	0.8648	0.9316	0.9002
−0.689	−0.689	−6.813	−2.730	−2.144	3.6102	4.0305	0.9284	0.8803	0.8803	0.9396	0.9001
1.367	−3.645	−5.961	−2.746	−2.049	3.6087	4.0314	0.9272	0.8648	0.9043	0.9316	0.9002
1.760	−5.143	−4.913	−2.765	−1.954	3.6073	4.0324	0.9259	0.8628	0.9161	0.9221	0.9003
1.596	−6.426	−3.516	−2.782	−1.857	3.6059	4.0333	0.9246	0.8655	0.9259	0.9100	0.9005
−0.393	−7.618	−0.393	−2.801	−1.762	3.6046	4.0342	0.9233	0.8836	0.9346	0.8836	0.9006

of $P^2_{s_2s_5}$, $P^2_{s_2s_6}$, and $P^2_{s_2s_7}$. [e] The average of $J_{C_1H_5}$, $J_{C_1H_6}$, and $J_{C_1H_7}$. [f] The sum of the diagonal density matrix elements for atom C_1. [g] The average of q_{H_5}, q_{H_6}, and q_{H_7}.

a cis arrangement is maintained between H_8 and H_4 and between H_4 and H_5.

In addition to showing the computed couplings, Table I gives the computed values of atomic valence-shell electron densities and values of certain "bond orders" (*e.g.*, $P^2_{s_2s_5}$) between the valence-shell s orbitals centered on coupled nuclei. It is the bond orders which carry in a simple MO calculation the sense of the hybridization (or per cent s character), a view that has been so popular in interpreting carbon coupling constants, especially J_{CH}.[18,19] The relationship is manifested in the early McConnell equation.[20] This is

$$J_{AB} = (4/3)^2 h\beta^2 \gamma_A \gamma_B (\Delta E)^{-1} s_A{}^2(0) s_B{}^2(0) P^2_{s_As_B} \quad (2)$$

shown in eq 2, where the "mean excitation energy," ΔE, results from an approximation characteristic of perturbation theories at that level. It is the assumed constancy of the product $(\Delta E)^{-1} s_A{}^2(0) s_B{}^2(0)$, for simple hydrocarbons, that leads to interpretations based on carbon s character *via* the $P^2_{s_As_B}$ term, an assumption that has been criticized on theoretical grounds.[21-23]

In addition to individual spin–spin couplings, electron densities, and bond orders, Table I contains the averages of values calculated for the three hydrogen atoms of a methyl group. Such averages are meant to sim-

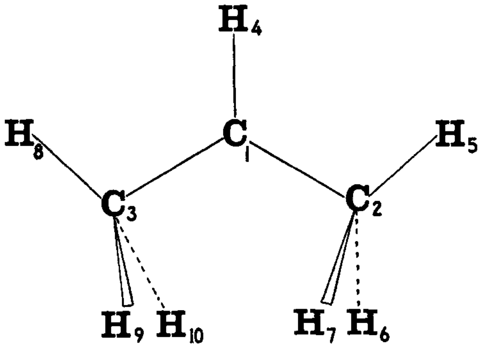

Figure 1. Geometry notation for structural variations. The atoms H_8, C_3, C_1, H_4, C_2, and H_5 are taken to be in the same plane. Methyl groups are assigned tetrahedral angles and C–H bond distances of 1.09 Å. The C_1H_4 bond distance is 1.08 Å and the CC bond distances are 1.52 Å. The angle $\alpha = \angle H_4C_1C_3 = \angle H_4C_1C_2 = \angle C_3C_1C_2$.

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ulate the corresponding values, numbers that could be expected for an experimental case in which the methyl groups rotate sufficiently rapidly that individual methyl hydrogen orientations cannot be identified separately.

Table II presents calculated results on the same set of variables for alterations of C_1–H_4 and for C_1–C_2 and C_1–C_3 bond lengths in the basic trigonal configuration. Table III presents the results of varying the dihedral angles $\angle H_4C_1C_2H_5$ and $\angle H_4C_1C_3H_8$ in phase (both H_8 and H_5 above or below the carbon plane) for the otherwise "standard" geometry.

Discussion

Table I. Focusing attention first upon the directly bonded couplings $J_{C_1H_4}$ and $J_{C_1C_2}$, we see from Table I that progression from the trigonal to tetrahedral C_1 configuration sends the two couplings in opposite directions, $J_{C_1H_4}$ increasing by about 20% while $J_{C_1C_4}$ decreases by about the same percentage. However, the calculated values of $P^2{}_{s_1s_4}$ vary almost negligibly over this same variation. This seems to cast doubt on the validity of any conclusions to be drawn about variations in carbon s character from variations in the J_{CH} values of a hydrogen atom and a nominally "positive" carbon atom to which it is attached, if these variations are due to angular distortions about the three-coordinate carbon. A somewhat closer relationship exists between the variations in $J_{C_1C_2}$ and $P^2{}_{s_1s_2}$, although the fractional variations in the latter still correspond only to about half of that in the former.

The J_{CH} values within a methyl group experience a small variation for $J_{C_2H_5}$ and rather large variations in opposite senses for $J_{C_2H_6}$ and $J_{C_2H_7}$. The corresponding $P^2{}_{s_Cs_H}$ values exhibit monotonic changes, but these are not proportional to the corresponding J_{CH} variations in any of the three cases. The calculated average J_{CH} for the methyl group increases significantly in the trigonal-to-tetrahedral variation, while the corresponding average $P^2{}_{s_Cs_H}$ value decreases slightly.

Some of the largest absolute variations, and certainly the largest fractional variations, occur with the geminal J_{C_1H} values, both for the individual couplings and for their averages. Each individual coupling and the average change sign throughout the range of α values. The variation of the average is dominated by changes in $J_{C_1H_5}$. Variations in the computed $J_{C_2H_4}$ values are rather small, presumably because of the constraint that maintains the cis relationship between atoms H_4 and H_5, and which maintains a relatively constant relationship between the C_2H_5 bond and the "vacant C_1 hybrid orbital." While there is a monotonic relationship between $J_{C_1H_6}$ and $P^2{}_{s_1s_2}$, there seems to be no simple general relationship between the ${}^2J_{CH}$ values and the s character in the C_1C_2 bond, as had been suggested.[24] There is earlier evidence that this relationship is not general.[25]

Inspection of the electron density values given in Table I shows that rather small changes accompany the geometrical alteration. Especially small is the variation of the *average q* for methyl hydrogens.

Table II. The calculated results of the table show relatively small variations for most parameters. However, within the sets constituted by the first three rows, the second three rows, or the last three rows, it is seen that extending the C_1–H_4 bond causes a significant *increase* in the calculated $J_{C_1H_4}$ values. Also, there is an anticorrelation with the $P^2{}_{s_1s_4}$ values within each of these three sets. The inverse of such a relationship between J_{CH} and R_{CH} has been suggested previously on experimental grounds.[18a,26] Similarly, for fixed values of $R_{C_1H_4}$, increasing the C–C bond distance causes an increase in the calculated J_{CC} values, and again there is an anticorrelation with $P^2{}_{s_1s_2}$.

The calculated J_{CH} values for the methyl groups are seen to be essentially insensitive to the C_1–H_4 bond length. However, they are seen to increase significantly with increasing CC bond lengths, and these increases are paralleled by increases in $P^2{}_{s_2s_H}$ values.

The small variations in geminal J_{C_1H} and J_{C_2H} values are seen to be correlated monotonically with $P^2{}_{s_1s_2}$ values, both for variations of $R_{C_1H_4}$ and for variations of $R_{C_1C_2}$. However, except for the relationship between geminal J_{C_1H} values and $P^2{}_{s_1s_2}$ for R_{C-C} variations, the fractional variations of the $P^2{}_{s_1s_2}$ values are much smaller than those of the calculated geminal J_{CH} values. There are no changes in sign of the calculated geminal C–H couplings for these bond-length variations.

The main pattern that emerges from the electron density values in Table II is the consistently lower value of q_{H_6} (and q_{H_7}) compared to q_{H_5}. This reflects the hyperconjugative interaction between the "vacant" C_1 π orbital, and the out-of-plane hydrogens, an interaction intimately involved in determining geminal J_{C_1H} values.[27]

Table III. Inspection of this table reveals that calculated results involving only the atoms C_1, C_2, H_4, and H_{567}(average) are largely insensitive to rotation of the methyl groups. Only parameters involving H_5 or H_6 or H_7 individually show substantial variations, and these variations are quite pronounced. The q_{H_5} values show a minimum at about $\phi = 90°$, corresponding to the maximum conjugation between H_5 and the vacant orbital of C_1. At the same value of ϕ it appears that $J_{C_1H_5}$ has its maximum value and $J_{C_2H_5}$ reaches a minimum (but not $P^2{}_{s_2s_5}$). Details of the dependence of geminal J_{CH} values upon conformational relationships to conjugation centers will be discussed elsewhere.[27]

Summary and Conclusions

The coupling constants between the central carbon and the directly bonded carbons or hydrogen are sensitive to variations in the bond angles and bond lengths defining the positions of those atoms. The coupling constants involving methyl hydrogens are particularly sensitive to the central bond angles and to the conformational orientation of the methyl group. However, the *averages* of the coupling constants involving those hydrogens are highly sensitive to neither methyl confor-

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(24) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Elmsford, N. Y., 1966, p 1027.

(25) G. J. Karabatsos and C. E. Orzech, *J. Amer. Chem. Soc.*, **86**, 3574 (1964).

(26) K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Scherthler, and J. Lavanish, *Tetrahedron*, 21, 2749 (1965).

(27) G. E. Maciel, manuscript in preparation.

mation nor central bond lengths, but depend markedly upon central bond angles.

Simple interpretations in terms of s–s bond orders, related to the popular "carbon-s-character" approach, do not appear to hold in all cases, even qualitatively. The results given in the tables are not meant to provide specific numbers to compare with actual data, but rather to suggest the trends in couplings to be expected for certain geometrical alterations.

Acknowledgment. The author wishes to thank the Applied Sciences Department for their assistance.

Solvent Effects in Coordination Kinetics. I. Inner-Sphere Effects in the Reaction of Solvated Nickel(II) Ion with Ammonia in Methanol–Water Mixtures

W. J. MacKellar and D. B. Rorabacher*

Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. *Received November 6, 1970*

Abstract: The kinetics of solvated Ni(II) ion reacting with ammonia have been studied using the temperature-jump relaxation method in methanol–water mixtures ranging from 0 to 99% methanol (by weight). The ammonia protonation constants and Ni(II)–ammine stepwise stability constants have also been determined in each solvent composition studied. The kinetic results show a distinct maximum in the formation rate constant for the nickel(II)–monoammine complex in the vicinity of 80–90% methanol. In conjunction with Ni(II) solvation measurements, these results indicate that $Ni(H_2O)_5(CH_3OH)^{2+}$ (5:1 species) is the most labile species of solvated Ni(II) ion in these solvents. The rate constant for nickel–methanol bond rupture in this species is then estimated to be $k_{5:1}{}^{Ni-CH_3OH} = (7\text{–}8) \times 10^5\ sec^{-1}$, approximately 800 times larger than the rate constant established for the same bond rupture in $Ni(CH_3OH)_6{}^{2+}$ and 20 times larger than the rate constant for nickel–water bond rupture in $Ni(H_2O)_6{}^{2+}$. A general theory is proposed in terms of the dissociative mechanism to account for the kinetic behavior of all labile solvated metal ions in both pure and mixed coordinating solvents.

Alcoholic solvents were first applied to the kinetic studies of coordination reactions in order to permit the use of low temperatures for slowing down reactions which were considered "instantaneous" in water.[1] Currently, the use of such nonaqueous solvents has come under renewed interest as a means of investigating the role of the solvent itself in influencing reaction rates.

The dissociative mechanism proposed by Eigen to explain the kinetic behavior of aqueous complex formation reactions[2] predicts a multifaceted role for the solvent in influencing reaction rates. As generalized here for any labile octahedrally solvated metal ion

$$MS_6{}^{a+} + L^{b-} \overset{K_{os}}{\rightleftharpoons} \underset{\substack{\text{outer-sphere}\\ \text{complex}}}{MS_6{}^{a+}\cdots L^{b-}} \xrightarrow[\text{rate-determining step}]{k^{M-S}}$$

$$\underset{\substack{\text{short-lived}\\ \text{intermediate}}}{MS_5{}^{a+}\cdots L^{b-}} \xrightarrow{\text{(fast)}} MLS_5{}^{(a-b)+} \qquad (1)$$

This mechanism involves the rupture of a metal–solvent coordinate bond (designated by the rate constant k^{M-S}) as the rate-determining step to form a short-lived intermediate of lower coordination number, MS_5, followed by rapid insertion of a nearby ligand into the vacated coordination site.

The short lifetime indicated for the MS_5 species requires that the entering ligand must be in the second coordination sphere (outer sphere) at the time of the metal–solvent bond rupture in order to compete successfully with the surrounding solvent molecules for the vacant site. As a result, the extent of outer-sphere complex formation, also dependent on the properties of the solvent matrix, directly influences the reaction rate. Thus, the observed overall formation rate constant, $k_M{}^L$, can be equated to the product of the outer-sphere equilibrium constant, K_{os},[3,4] and the rate constant for metal–solvent bond rupture, *viz.*

$$k_M{}^L = K_{os}k^{M-S} \qquad (2)$$

both of the terms on the right being solvent dependent. The general dissociative mechanism is represented pictorially in Figure 1.

The weaker coordinating ability of alcoholic oxygen as a donor atom compared to aqueous oxygen led to the initial speculation that, for octahedrally solvated metal ions such as Ni(II) ion, "a dissociative mechanism in which $Ni(H_2O)_5{}^{2+}$ and $Ni(CH_3OH)_5{}^{2+}$ are formed should *always be more rapid for methanol than for water.*"[5] Evidence from nmr studies, however, indicates that the reverse order is observed for solvent-exchange reactions when pure solvents are involved, *i.e.*,

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