The Molecular Structures and Thermodynamic Functions of 2-Methylbutane and 2,3-Dimethylbutane

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Abstract: Previous values of the stabilities of the conformational isomers of 2-methylbutane and 2,3-dimethylbutane as inferred from the Raman spectra and the thermodynamic functions of these compounds have not been in accord with conformational concepts as expressed by the number of gauche (skew methyl) interactions. Recent Raman studies have removed some previous ambiguities and have resulted in improved values of the conformational isomer stabilities which show that they cannot be accounted for in terms of numbers of gauche interactions alone. Further, the redetermined stability of the 2-methylbutane conformers is not in accord with previous interpretation of the thermodynamic functions. In the present work, we show that the isomer stabilities, the thermodynamic functions, and the conformational energy minimization calculations are all in reasonable mutual accord. It is emphasized that valence angle distortion is important in reducing gauche strain and accounts for the lack of correlation with the number of gauche interactions.

Interest in the interpretation and prediction of the conformational properties of complex organic molecules and polymers has focused a great deal of attention on the properties of those relatively few simple molecules whose properties have been studied thoroughly experimentally. Obviously, methods for property prediction must work well on these "test" molecules if we are to have confidence in predictions on more complex molecules. Two examples of the apparent failure of current qualitative concepts of hydrocarbon structure have been the properties of 2-methylbutane and 2,3-dimethylbutane. The series *n*-butane, 2-methylbutane, and 2,3-dimethylbutane each should have two conformational isomers. The conformers of each molecule differ by one gauche (skew methyl) interaction (see Table I and Figures 1, 2, and 3). Hence, the difference in energy between each isomer pair should, on this basis, be nearly the same. In the case of *n*-butane, it has been known for some time that both the intensity of the Raman vibrational bands[1] and the thermodynamic functions[2] (S^0 and $C_p{}^0$) are in accord with the gauche isomer being ~800 cal more energetic than the trans. This value along with values[3] from *n*-pentane and *n*-hexane forms the basis of much of the current interpretation of hydrocarbon conformational properties. However, the situation with respect to 2-methylbutane and 2,3-dimethylbutane has been perplexing. In earlier work, the Raman spectrum of 2-methylbutane indicated an energy difference of ~100 cal between conformers.[4] However, from analysis of the thermodynamic functions (S^0, $C_p{}^0$) Scott et al.[5] concluded that the C_s isomer was of much higher energy (at least several kilocalories) than the C_1 form. For 2,3-dimethylbutane Szasz and Sheppard[4] found no temperature sensitive conformer bands from which it was concluded that either one isomer was of much higher energy or that both existed in equal population ($\Delta H = 0$). Scott et al.[5] concluded from the thermodynamic functions that both conformers have the same energy. Allinger et al.[6] on the basis of conformational energy calculations predicted that the isomers should be of nearly equal energy. They pointed out the importance of valence angle distortion in determining conformer stabilities.

The advent of laser Raman spectroscopy has made a much more careful analysis of the spectrum possible. Verma, Murphy, and Bernstein[7] have recently restudied the temperature dependent conformer bands in 2-methylbutane and have found such bands in 2,3-dimethylbutane allowing them to assign energy differences between conformational isomers (see Table I). They also have redetermined the energy difference in *n*-butane. They find a systematic drop in ΔH through the series with the isomers of 2,3-dimethylbutane being of nearly comparable energy. In confirmation of the latter, they find the ratio of intensities of the two forms to be ~2 to 1 in agreement with the statistical weights. The crystalline phase band corresponds to the less intense liquid band as is consistent with it being due to the more symmetrical C_{2h} form. In summary then, the situation seems to be that for 2-methylbutane the previous interpretation of the thermodynamic functions is not consistent with the new Raman results. For 2,3-dimethylbutane the energy difference between conformers is now unambiguously settled in favor of nearly equally stable forms. This energy difference is anomalously low in the context of gauche interactions but is consistent with conformational energy calculations in which all internal degrees of freedom are allowed to participate.

In view of these new data that have removed the previous experimental ambiguities and the crucial importance of these well-studied molecules as test cases for predictive methods, it now seems appropriate to undertake a unified critical comparison of the relationships among the conformer stabilities, thermodynamic functions, and results of conformational energy mimimization calculations. This is the purpose of the present paper.

Calculations

Energy minimization calculations were carried out using previously developed algorithms.[8,9] The parameters with one exception have been reported earlier.[10] The exception is an adjustment to the intrinsic rotational barrier. Recent work with barriers[11] had shown that our previous intrinsic barrier is a bit low and in the present work we have increased it by 20% from 2.1 to 2.5 kcal/mol. The latter gives a total barrier of 2.8 kcal/mol for ethane. Calculated energy differences reported by Allinger and his coworkers[6] using their parameters are also listed.

In order to evaluate the thermodynamic functions, the vibrational frequencies are required. Calculated values of these are also available from the minimization algorithm.[8] The calculated frequencies are listed in Table II along with observed frequencies. The latter are principally those reported by Snyder and Schachtschneider.[12a,b] A few comments concerning our calculated frequencies are in order. Snyder and Schachtschneider have shown[12a,b] that a proper set of transferable force constants leads to excellent agreement between calculated and observed frequencies for al-

Table I. Summary of Experimental and Calculated Conformer Energies

(1)	Conformational isomers (2)	No. of *gauche* (skew methyl) interactions (3)	ω^a (4)	ΔH(earlier) Raman (5)	ΔH(earlier) Thermodynamic functions (6)	ΔH(recent Raman)^f (7)	ΔH (conf calcd.)^g (8)
n-Butane	*Trans*	0	1/2	770^b cal/mol	800^d cal/mol	966 ± 54 cal/mol	675 (730) 670 cal/mol
	Gauche	1	2/2				
2-Methylbutane	C_1	1	2/1	100^c	>2000^e	809 ± 50	588 (640) 440
	C_s	2	1/1				
2,3-Dimethylbutane	C_{2h}	2	1/2	0 or >1000^c	0^e	54 ± 30	201 (250) 80
	C_2	3	2/2				

^{a} Statistical weight (number of stereo isomers divided by rotational symmetry number). ^{b} Reference 1. ^{c} Reference 4. ^{d} Reference 2. ^{e} Reference 5. ^{f} Reference 7. ^{g} From conformational energy minimization calculations. The first value is from this work, the value in parentheses is the first value corrected for zero-point and vibrational energy (ref 10), the third value is from ref 6.

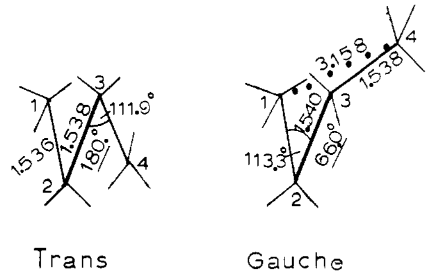

Figure 1. Calculated structures of conformers of *n*-butane. In Figures 1-3 torsional angles are underlined, are based on atoms 1, 2, 3, and 4, and are based on eclipsed as $\phi = 0°$. In *gauche n*-butane both torsional angle adjustment (from 60 to 66.0°) and valence angle adjustment (both 1, 2, 3 and 2, 3, 4) contribute to increasing the nonbonded distance (1, 4) and reducing methyl···methyl repulsion.

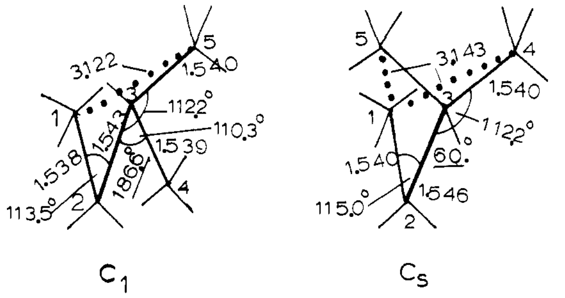

Figure 2. Calculated structures of conformers of 2-methylbutane. In the C_1 form, torsional angle adjustment (from 180° to 186.6°) assists in increasing the methyl···methyl (1, 5) distance but only one valence angle adjustment (1, 2, 3) can assist. Thus, the methyl···methyl distance is less and the repulsion greater than in *gauche-n*-butane (see Figure 1). Although torsional adjustment is not possible in the C_s form, methyl-methyl distances (1, 5 and 1, 4) greater than in the C_1 form result from valence angle (1, 2, 3) adjustment to 115°.

kanes (about 1% overall). To achieve this agreement, they found it necessary to include interaction force constants, especially between bending and stretching. Our conformational energy force field does not include (valence) interaction constants and therefore our overall agreement with the observed frequencies is not as good. However, the largest discrepancies involve principally various C-H bending motions with frequencies above 1000 cm^{-1}. The thermodynamic functions are relatively insensitive to these and our calculated values are quite satisfactory. The thermodynamic functions are most sensitive to the low frequency torsional motions.

The methyl torsional frequencies are sensitive to differences in nonbonded interactions in different conformations. The Snyder-Schachtschneider force field does not include nonbonded interactions and thus does not accurately reflect the effect of steric interactions on methyl torsional frequencies. Since there was little experimental information on such frequencies available to them, this inadequacy was not apparent in the overall accuracy of their calculated frequencies. In Table II calculated frequencies for both the Snyder-Schachtschneider force field and ours are compared with the observed frequencies for propane. Experimental values of the methyl torsional frequencies are now available for the latter from neutron diffraction.[13] The above mentioned points of the superiority of the (valence) interaction constant containing force field in the middle frequency region and the superiority of our nonbonded interaction containing force field for the methyl torsions are illustrated by this molecule.

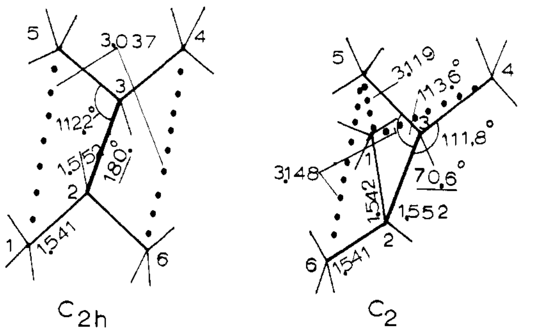

Figure 3. Calculated structures of conformers of 2,3-dimethylbutane. In the C_{2h} form, methyl···methyl distances (1, 5 and 4, 6) are exceptionally short since alleviation by torsional adjustment or by valence angle adjustment is not possible. In the C_2 form, torsional angle adjustment increases distances (1, 4) and (5, 6). The otherwise shortened 1, 5 distance is increased by adjustments of valence angles (1, 2, 3) and (2, 3, 5).

The calculated frequencies together with the calculated moments of inertia were used to calculate the thermodynamic functions for each conformer. The functions for the torsional vibrations were corrected for anharmonicity using the tables of Pitzer.[14] The required barrier heights were calculated from the harmonic frequencies and the effective moments of inertia. The conformer functions were then combined to obtain the thermodynamic functions of the equilibrium mixture of conformers by methods previously described.[9] The equilibrium mixture calculation requires the enthalpy difference between conformers. The calculation was carried out for both the observed (column 7) and calculated (column 8) ΔH values of Table I. Both sets of resulting thermodynamic functions are listed in Table III. In the case of 2-methylbutane, the value of $\Delta H = \infty$(>2000 cal) proposed by Scott et al.[5] is also included. The observed values are shown also. The values for 2-methylbutane and 2,3-dimethylbutane are those tabulated by Scott et al.[5] For 2-methylbutane they are based on the experimental values of Scott et al.[5] for $C_p{}^0$(gas) and $\Delta H_{\text{vap}}{}^0$ and the values of

Table II. Calculated and Observed Vibrational Frequencies (cm^{-1})[a]

Propane			
Calcd.	Obsd.	Calcd.	Obsd.
A_1 2974 (2966)[b]	2965	B_1 2971 (2963)	2965
2872 (2882)	2875	2865 (2882)	2875
2855 (2856)		1561 (1465)	1464
1493 (1471)	1473	1412 (1367)	1370
1421 (1445)	1449	1370 (1342)	1332
1404 (1378)	1385	1000 (1046)	1049
1064 (1151)	1157	929 (924)	921
851 (870)	868	B_2 2973 (2965)	2965
388 (382)	375	2925 (2921)	2915
A_2 2973 (2964)		1444 (1464)	1459
1441 (1459)		1053 (1185)	1187
1200 (1279)	1278	774 (747)	748
970 (903)	899	259 (220)	265 ± 8[c]
212 (200)	217 ± 8[c]		

trans-n-Butane			
Calcd.	Obsd.	Calcd.	Obsd.
A_g 2973	2965	B_g 2973	2965
2872	2872	2926	2912
2859	2853	1444	1460
1593	1462	1203	1300
1465	1455	1038	
1412		846	
1403		249	
1080	1148	B_u 2972	2965
968	1053	2867	2875
864	835	2853	2861
394	427	1510	1468
A_u 2973	2965	1421	1459
2922	2920	1406	1375
1442	1455	1331	1293
1216	1257	991	1010
999	944	954	965
727	733	297	
224			
119			

gauche-n-Butane				C_1 2-methylbutane				C_s 2-methylbutane	
Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.[d]	Calcd.[d]
A 2974		B 2973		2974		1400	1351	A' 2975	298
2972		2971		2973		1345	1337	2971	230
2925		2923		2973		1304	1298	2971	A'' 2974
2872		2868		2972		1220	1268	2897	2972
2860		2854		2972		1113	1176	2870	2971
1576		1529		2970		1073		2864	2923
1473		1440		2923		1066	1149	2858	2865
1450		1417		2897		1014	1037	1570	1549
1410		1404		2869		1000	1011	1516	1452
1398		1368		2865		970	969	1462	1438
1210	1282	1207	1233	2864		967	952	1445	1410
1063	1167	1027	1133	2857		941	917	1420	1341
1023	1077	994		1584		904	910	1415	1209
983	981	937	956	1544		827	796	1397	1066
854	835	752	747	1503		758	764	1345	1014
777	789	449		1464		443	459	1110	972
329	325	213		1448		419		1069	940
274				1444		361	368	1010	770
110				1442		292		961	375
				1417	1384	255		896	275
				1414	1377	227		760	207
				1410	1366	212		531	87
						93		388	

C_{2h} 2,3-dimethylbutane				C_2 2,3-dimethylbutane						
Calcd.[d]	Calcd.	Obsd.	Calcd.[d]	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.[d]	Calcd.	Obsd.
A_g 2974	A_u 2972		B_g 2971	B_u 2973		A 2975		931	1410	
2973	2970		2968	2972		2973		746	1352	
2899	2865		2863	2892		2972		454	1284	1297
2866	1533		1561	2865		2970		343	1082	1168
1571	1456		1439	1496		2897		308	1063	1103
1471	1409	1368	1412	1442		2866		274	1021	1038
1449	1306	1304	1350	1417	1377	1569		234	970	
1403	1053	1067	1079	1292	1278	1549		67	940	910
1137	969	956	972	1089	1155	1457			877	835
1069	941	918	938	1019	989	1447		B 2974	537	
932	314		401	870	871	1445		2972	412	
799	219		207	421		1416		2971	298	
481	65			360		1409		2970	242	
372				223		1341	1297	2894	209	
248						1139	1199	2866		
						1088	1161	2863		
						1045	1029	1501		
						976	954	1548		
						942		1455		
								1437		
								1419		

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[a] Observed frequencies are from ref. 12a and 12b except where noted. [b] Calculated values from force field using interaction constants (ref 12b). [c] Methyl torsional frequency from neutron diffraction (ref 13). [d] No observed values.

Guthrie and Huffman[15] for S^0(liquid). For 2,3-dimethylbutane they are based on the results of Waddington et al.[16] for C_p^0(gas) and ΔH_{vap}^0 and those of Douslin and Huffman[17] for S^0(liquid). For comparison the calculated and experimental[18] functions for *n*-butane are also shown.

Table III. Calculated and Observed Thermodynamic Functions[a]

T	$-(G^0 - G_0^0)/T$	$(H^0 - H_0^0)/T$	S^0	C_p^0
		n-Butane[b]		
298.15	58.68	15.41	74.10	23.36
	58.44	15.42	73.86	23.76
	58.54	15.58	74.12	23.29
400.0	63.57	18.26	81.84	29.59
	63.34	18.35	81.70	29.86
	63.51	18.35	81.86	29.60
500.0	67.97	21.13	89.10	35.49
	67.76	21.24	89.00	35.67
	67.91	21.19	89.10	35.34
600.0	72.07	23.90	96.03	40.58
	71.88	24.08	95.97	40.71
	72.01	23.98	95.99	40.30
		2-Methylbutane[c]		
298.15	64.95	17.62	82.58	28.70
	64.90	17.42	82.52	28.56
	64.70	17.35	82.05	28.45
	64.36	17.75	82.12	28.39
400.0	70.66	21.46	92.12	36.58
	70.61	21.47	92.08	36.43
	70.33	21.20	91.53	36.41
	70.07	21.49	91.56	36.49
500.0	75.88	25.21	101.10	43.77
	75.84	25.02	101.07	43.81
	75.50	24.97	100.47	43.64
	75.28	25.24	100.51	43.71
600.0	80.81	28.81	109.63	49.90
	80.77	28.83	109.61	49.93
	80.39	28.59	108.98	49.79
	80.21	28.83	109.05	49.89
		2,3-Dimethylbutane[d]		
298.15	67.13	20.56	87.70	34.11
	67.48	20.25	87.74	34.01
	67.58	19.84	87.42	33.59
400.0	73.80	25.25	99.05	43.55
	74.08	25.00	99.08	43.51
	74.06	24.58	98.64	43.30
500.0	79.93	29.79	109.72	52.01
	80.15	29.58	109.54	51.99
	80.04	29.22	109.26	51.94
600.0	85.74	34.12	119.87	59.26
	85.93	33.95	119.88	59.05
	85.77	33.61	119.38	59.23

[a] All units are cal/°K/mol. At each temperature the values are calculated for the experimental and the calculated energy differences between conformers (see Table I columns 7 and 8). For 2-methylbutane, the value $\Delta H = \infty$ is also included. The values of ΔH used are indicated at the 298°K entries. [b] At each temperature row one is at $\Delta H = 730$, row two is at $\Delta H = 966$, and row three is the observed values. [c] At each temperature row one is at $\Delta H = 640$, row two is at $\Delta H = 809$, row three is at $\Delta H = \infty$, and row four is the observed values. [d] At each temperature row one is at $\Delta H = 250$, row two is at $\Delta H = 54$, and row three is the observed values.

Discussion

From comparison of columns 7 and 8 of Table I, it is apparent that although there is not exact agreement, the conformational energy minimization calculations reproduce reasonably well the features of conformer stabilities. It is of interest to emphasize why the concept of the number of gauche interactions determining stability fails. Since, in energy minimization calculations, simultaneous adjustments of all of the internal coordinates of the molecule are made and the total energy is the sum of a large number of individual energy functions, it is difficult to ascribe the overall result to any given structural feature. However, simple qualitative rationales can often be extracted from the details of the calculation. In the present examples, we point out the following. If the skeletal geometries all involved the same bond lengths and valence angles, and the torsional angles were at the exact 60, 180, 300° gauche, trans, gauche′ values, the energy function method would be essentially equivalent to counting gauche methyl interactions. The lack of correlation with the latter is the result of relatively modest adjustments in the valence and torsional angles. In *n*-butane (see Figure 1), the methyl···methyl nonbonded interactions[19] in the gauche conformation result in the minimum energy position of the skeletal torsional angle being displaced (in our calculation) from 60 to 66.0° and the valence angles (1, 2, 3 and 2, 3, 4) being increased over the trans to 113.3 from 111.9°. In 2-methylbutane this adjustment is possible for the torsional angle and one of the valence angles (1, 2, 3) (valence angle 2, 3, 5 does not increase due to hindrance from methyl group 4) in the C_1 form.

The torsional angle adjustment is not possible in the symmetrical C_s form (see Figure 2). Thus, it might be expected that the gauche–trans difference would be greater than in *n*-butane rather than less as is observed. However, in the C_s form an exceptionally large adjustment of the valence angle (1, 2, 3) results in an increase in the nonbonded distances and a reduction of the methyl···methyl repulsions between centers 1, 4 and 1, 5 to below that in the C_1 form. The large valence angle change appears to be possible because it alleviates two simultaneous gauche interactions.

Turning to 2,3-dimethylbutane, we see that in the C_{2h} form no adjustment of the skeletal torsional angle as in gauche *n*-butane or C_1 2-methylbutane is possible. Further, any adjustment of a valence angle would be hindered by the other methyl substituent on the center carbon (i.e., presence of methyl group 6 hinders changes in angle 1, 2, 3, etc.). Thus, the C_{2h} form is a relatively high-energy conformation for the number of gauche interactions it possesses. In contrast, in the C_2 form adjustment of the skeletal torsional angle reduces two methyl···methyl repulsions (1, 4 and 5, 6) and increases one (1, 5). However, simultaneous adjustments of the valence angles 1, 2, 3 and 2, 3, 5 are effective in reducing the 1, 5 repulsion. Just as in C_s 2-methylbutane, these valence angle adjustments are effective because each alleviates two gauche interactions. Thus, the overall effect of the lack of strain-relieving possibilities in the C_{2h} form and the presence of them in the C_2 form results in the two forms being of nearly equal energy in spite of the greater number of gauche interactions in the latter.

In discussing the thermodynamic functions, we will focus our attention on the entropy, S^0, and the heat capacity, C_p^0, as they are more or less independently measured quantities. The entropy, S^0, is derived from integrated condensed phase heat capacities down to low temperatures and heats of vaporization. The vapor heat capacity C_p^0 is independently measured. The entropy tends to be sensitive to both the vibrational frequencies and the population of conformers while C_p^0 is sensitive to vibrational frequencies but somewhat less sensitive to conformer population.

Scott et al.[5] estimate the uncertainty interval of their vapor-phase C_p^0 values for 2-methylbutane at ~0.3%, so an overall reliability of 0.1–0.2 cal/°K/mol is probably reasonable. For the liquid entropies, the uncertainties for 2-methylbutane and 2,3-dimethylbutane were estimated at ±0.1 and ±0.14 cal/°K/mol, respectively, by the investigators.[15,17] The overall uncertainty of the ideal gas entropies is likely to be of the order of 0.2–0.3 cal/°K/mol. Thus, it is seen in Table III that good agreement is obtained between calculated and observed values of S^0 and C_p^0 for *n*-butane for both values of ΔH used. For 2-methylbutane the agreement is good for C_p^0 for all three of the ΔH values calculated. For S^0 the agreement is certainly better for $\Delta H = \infty$ in accord with Scott et al.[5] However, conversely we are not prepared to say that the discrepancy of 0.5 cal/°K/mol for ΔH = 600–800 cal/mol is significant in the light of experimental uncertainties and uncertainties in the calculated values. For 2,3-dimethylbutane the situation is similar, the C_p^0 values are in good agreement, and the calculated entropies are a bit high but probably not significantly so in view of the uncertainties.

In summary, it appears that the stabilities of the conformers of 2-methylbutane and 2,3-dimethylbutane are consistent with conformational energy calculations and have a simple qualitative explanation in terms of valence and torsional angle adjustments. Further, the stabilities are in reasonable accord with the thermodynamic functions.

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(19) D. H. Wertz and N. L. Allinger have recently (*Tetrahedron*, **30**, 1579 (1974)) proposed that gauche H···H nonbonded interactions play a dominant role in the structure of conformational isomers. In our parameterization, at least, they play a relatively minor role. In *gauche*- vs. *trans-n*-butane for example, we find methyl···methyl nonbonded interactions contribute 0.50 kcal/mol to the gauche–trans energy difference with other contributions to the total difference of 0.66 kcal/mol from the following sources of Me···H −0.30, H···H 0.16, torsional angle distortion 0.11, valence angle distortion 0.21, bond length distortion 0.03, and non-bonded interaction differences on the same side of the center C–C bond −0.05. It also seems clear that most of the torsional and valence angle distortional energies are due to the methyl···methyl repulsions.

A Study on the Interaction of Eu^{2+}(aq) with Pyridinecarboxylic Acids

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Abstract: Europous ion forms with isonicotinic, *N*-methylisonicotinic, nicotinic, and picolinic acids one to one complexes having several features, which are rather unusual for a lanthanide ion. They are formed in strongly acidic aqueous solutions and have absorption maxima around 420 nm. The formation constants are 0.15 l. mol^{-1} for nicotinic acid, 0.2 l. mol^{-1} for picolinic acid, 1.9 l. mol^{-1} for isonicotinic acid, and 0.4 l. mol^{-1} for *N*-methylisonicotinic acid, respectively. Evidence is presented that the complexes involve charge transfer from the metal ion to the ligand. The complexes of nicotinic and picolinic acids are stable toward further redox reaction. The complexes of isonicotinic acid and its *N*-methyl derivative, however, undergo further reduction leading in the first case to isonicotinaldehyde and in the second very likely to the dihydro derivative. In the presence of Eu^{3+}(aq) the kinetics of the redox reaction of isonicotinic acid and its *N*-methyl derivative are second order in europous ion, first order in the organic acid, first order in hydrogen ion, and inverse first order in Eu^{3+}(aq). A unified mechanism is proposed to explain the results for both of these acids, which is also consistent with the results obtained on complex formation and with the postulate of a charge transfer from europous ion to the ligand.

The mechanism of electron transfer *through* reducible organic ligands is related to the mechanism of transfer *to* such ligands. It must be recalled that even when these ligands are bound, the electron is very likely first transferred to them, before finding its way to the central ion.[2]

If the ligands are bound, the presence of the central metal ion makes it impossible to detect and study some important details of the electron transfer process. In the reactions of free ligands[3] with low valent metal ions some of these "missing aspects" become more pronounced and can be studied by conventional techniques. Focusing attention on substituted pyridine ligands, it is worth mentioning the following two such aspects. (i) In studies of electron transfer through substituted pyridine ligands[4] the electron may "reside" for a while on the ligand. The intermediate radical-complex is, however, difficult to detect. In the corresponding reactions of free ligands[5] complex formation and subsequent reaction are time-resolved, and the course of the reaction from the precursor complex to the products can be explored more effectively. (ii) Kinetically, the reactions between substituted pyridine complexes and reducing metal ions are generally quite simple. The ligand, whether bound[4] or free[6] essentially acts as a catalyst. The differences in the overall chemistry caused by changes of the substituents on pyridine are rather trivial.

In the corresponding free ligand reactions the products