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Deamination of 2-Methyl-2-propanamine Induced by Hydroxyl Radicals and Metal Ions: A Comparison between the Rates of β Elimination of Ammonia and Water

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The reactions of $^{\bullet}CH_2C(CH_3)_2NH_3^+$ with $Cu^+(aq)$ and $Cr(H_2O)_6^{2+}$ were studied using the pulse radiolysis technique. The formation of the unstable $[Cu^{II}-CH_2C(CH_3)_2(NH_3^+)]^+$ and $[(H_2O)_5Cr^{III}-CH_2C(CH_3)_2(NH_3^+)]^{2+}$ ions was observed in these reactions. These complexes decompose via β elimination of NH_3 to yield 2-methylpropene, ammonia, and $Cu^{2+}(aq)$ or $Cr^{3+}(aq)$. The rates of these β-elimination reactions are considerably slower than those of the analogous β-hydroxyl elimination. It is suggested that the rates of the β-elimination processes are correlated to the strengths of the C–O and C–N bonds, which are cleaved in these reactions. A valence-bond analysis coupled with some ab-initio SCF–MO computations explains the effect of protonation on these bond strengths.

Introduction

Reactions between free radicals and metal ions occur in homolytic metal-catalyzed oxidations of organic compounds as well as in many biochemical processes.[1] The mechanism of such processes is important, and a large number of mechanistic studies have been carried out so far.[1] Most of the data are consistent with the formation of an intermediate with a metal–carbon σ-bond in the first step. The chemical properties of these short-lived intermediates can be easily studied with the pulse radiolysis technique.[2]

Recently, it has been pointed out that the decomposition of a complex with a Cu^{II}–carbon σ-bond via a β elimination of ammonia is a much slower process than the analogous process involving β elimination of water,[3] although it is known that the bond energy of C–O is considerably larger than that of C–N.[4] The comparison between these two processes was done for cuprous ions reacting with $^{\bullet}CH_2CH_2OH$ and $^{\bullet}CH(COOH)CH_2NH_3^+$ (the radicals obtained via H abstraction from ethanol and β-alanine, respectively) in aqueous solutions.[3] As these two systems are not identical, and the reactions of $Cu^+(aq)$ and $Cr(H_2O)_6^{2+}$ with the radical obtained by H abstraction from 2-methyl-2-propanol ($^{\bullet}CH_2C(CH_3)_2OH$) had been studied in detail,[5-8] we have chosen to study the reactions of these metal ions with the corresponding amine. A comparison of the chemical properties of $[Cu^{II}-CH_2C(CH_3)_2X]^+$ and $[(H_2O)_5Cr^{III}-CH_2C(CH_3)_2X]^{2+}$, where X = OH or NH_3^+, was expected to yield a better understanding of the differences between the β elimination of ammonia and that of water. Since the results point out again that the β elimination of ammonia is surprisingly a relatively slow process, it was decided to analyze this aspect also theoretically.

The mechanism of the decomposition of many organometallic complexes via a β-hydroxyl elimination has been studied in detail in many systems.[3,5-11] However, our knowledge of the mechanism of the decomposition of complexes with a metal–carbon σ-bond via a β-amino or β-phospho elimination processes is limited. These processes are very interesting from the biological point of view, as it has been found that cleavage of the histone main chain occurs through the deamination of intermediates formed by the addition of e_{aq}^- to the peptide–carbonyl bond.[12] In addition, DNA strand cleavage has been shown to result via scission of the phosphate ester bond of free-radical intermediates formed through the reaction of DNA with $OH^{\bullet}$ radicals.[13] The latter reaction was studied with D-ribose-5-phosphate as a model system for DNA, and it has been shown that the amount of dephosphorylation increased by about 8-fold in the presence of Fe(II) ions.[14] Thus, it is of great importance to study the physical and chemical properties of intermediates with a metal–carbon σ-bond, especially those which decompose through a β-elimination reaction, as similar reactions might lead to irreversible biological damage.

Experimental Section

Materials. All chemicals employed were of analytical grade. Solutions were prepared with distilled water which was further purified using a Milli-Q water purification system. Cuprous solutions were prepared by dissolving $Cu(CH_3CN)_4PF_6$ (Aldrich) in deaerated solutions. The pH was adjusted by adding $HClO_4$ before adding the cuprous salt. Solutions of 0.5 M chromium(II) perchlorate were prepared by dissolving high purity grade chromium powder in 1 M $HClO_4$ under helium atmosphere and then diluting to 0.01 M as previously described.[8] Portions of 5–20 mL of the latter solutions were transferred to 100-mL syringes containing the required organic solute and $HClO_4$ in N_2O-saturated solutions.

Irradiation. Pulse radiolysis experiments were carried out with the Varian 7715 linear accelerator at the Hebrew University of Jerusalem. The pulse duration was 0.5–1.5 μs with a 200-mA current of 5-MeV electrons. Irradiations were carried out in a 4-cm Spectrosil cell using three light passes. A 150-W xenon arc produced the analyzing light. The detection system included a Bausch & Lomb grating double monochromator, Model D330/D331 Mk.II, and an IP28 photomultiplier. The signal was transferred through a Sony/Tektronix 390AD programmable digitizer to a micro PDP-11/24 computer which operated the whole system. N_2O-saturated solutions containing 1 mM KSCN were used for dosimetry. The yield of $(SCN)_2^-$ was measured assuming $G((SCN)_2^-)$

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(1) (a) Kochi, J. K. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, Chapter 11. (b) Walling, C. *Acc. Chem. Res.* **1975**, *8*, 125. (c) Sheldon, R. A.; Kochi, J. K. *Metal Catalysis Oxidations of Organic Compounds*; Academic Press: New York, 1981. (d) Halpern, J. *Pure Appl. Chem.* **1982**, *15*, 238. (e) Espenson, J. H. In *Inorganic and Bioinorganic Mechanisms*; Sykes, A. J., Ed.; Academic Press: London, 1982; Vol. 1, p 1.

(2) (a) Meyerstein, D. *Acc. Chem. Res.* **1978**, *11*, 43. (b) Meyerstein, D. *Pure Appl. Chem.* **1989**, *61*, 885.

(3) Goldstein, S.; Czapski, G.; Cohen, H.; Meyerstein, D. *Inorg. Chim. Acta*, in press.

(4) (a) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. (b) Sanderson, R. T. *Chemical Bonds and Bond Energy*, 2nd ed.; Academic Press: New York, 1976.

(5) Freiberg, M.; Meyerstein, D. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1838.

(6) Buxton, G. V.; Green, J. C. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 697.

(7) Cohen, H.; Meyerstein, D. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 417.

(8) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1974**, *13*, 2434.

(9) Cohen, H.; Meyerstein, D.; Shusterman, A. J.; Weiss, M. *J. Am. Chem. Soc.* **1984**, *106*, 1876.

(10) Goldstein, S.; Czapski, G.; Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1988**, *27*, 4130.

(11) Sorek, Y.; Cohen, H.; Meyerstein, D. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 3431.

(12) Inami, O.; Kuwabara, M.; Hayashi, M.; Yoshi, G.; Syuto, B.; Sato, F. *Int. J. Radiat. Biol.* **1986**, *49*, 47.

(13) *The Chemical Basis of Radiation Biology*; von Sonntag, C., Ed.; Taylor & Francis: London, New York, Philadelphia, 1987.

(14) Stetler, L.; von Sonntag, C.; Schulte-Frohlinde, D. *Int. J. Radiat. Biol.* **1976**, *29*, 255.

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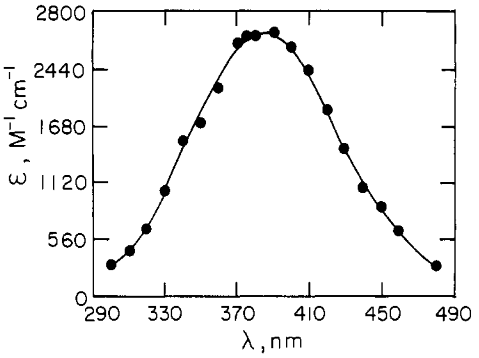

Figure 1. Absorption spectrum of $[Cu^{II}–CH_2C(CH_3)_2(NH_3^+)]^+$ formed in a pulse-irradiated N_2O-saturated solution containing 91 μM Cu^+(aq), 5×10^{-4} M $CuSO_4$, and 0.1 M 2-methyl-2-propanamine at pH 3.

= 6.1 and $\epsilon_{475} = 7600$ M^{-1} cm^{-1}. Between 1 and 10 pulses (3–30 krd) were delivered into small cylindrical glass bulbs (12-mL volume) filled with deaerated solutions and sealed with a rubber septum for analyzing the gaseous products.

Analysis. The gaseous products of the reaction of Cu^+(aq) and $Cr(H_2O)_6^{2+}$ with the radicals obtained from 2-methyl-2-propanamine and 2-methyl-2-propanol were analyzed by gas chromatography using a Hewlett Packard Model 5890 instrument. The gas samples were taken through the rubber septa with gastight syringes and were separated on a 10 ft × $^1/_8$ in. stainless steel column packed with Poropak Q 80/100 mesh at 180 °C. The gases were transferred through TCD and FID detectors connected in series. Calibration curves were obtained in order to determine quantitatively the amount of 2-methylpropene formed using irradiated N_2O-saturated solutions containing 1 mM $Cr(H_2O)_6^{2+}$ and 0.2 M 2-methyl-2-propanol at pH 3. Under these conditions all the primary radicals produced by the radiation are converted into $^{\bullet}CH_2C(CH_3)_2OH$, which reacts with $Cr(H_2O)_6^{2+}$ to yield Cr^{3+}(aq) and 2-methylpropene.[8,9]

Spectroscopic measurements were carried out using a Hewlett-Packard HP 8452A diode array spectrophotometer. The initial concentration of cuprous ions was determined with the use of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonic acid (bathocuproinedisulfonic acid).[15] This compound is very soluble in water, and complete formation of the Cu(I) complex occurs over the range pH 3–11. The complex is bichelate, it is not oxidized by oxygen, and its $\epsilon = 12\,250$ M^{-1} cm^{-1} at 483 nm. The results show that the initial concentration of cuprous ions was about 65%. This may indicate that the cuprous salt contains some cupric ions and also that Cu^+(aq) disproportionates to Cu^0 and Cu^{2+}(aq).

Production of Transients with a Metal–Carbon σ-Bond. Upon pulse irradiation of N_2O-saturated solutions containing high concentrations of an aliphatic compound (RH), the aliphatic free radical is formed within the pulse duration:

$$H_2O \rightarrow e_{aq}^-(2.75),\ OH^{\bullet}(2.75),\ H^{\bullet}(0.60),\ H_2(0.45),\ H_2O_2(0.75) \qquad (1)$$

The numbers in parentheses are *G* values which represent the number of molecules formed per 100 eV of energy absorbed in the solution.

$$e_{aq}^- + N_2O \xrightarrow{H_2O} N_2 + OH^- + OH^{\bullet} \qquad k_2 = 9.1 \times 10^9\ M^{-1}\ s^{-1}\ {}^{16} \qquad (2)$$

$$e_{aq}^- + H^+ \rightarrow H^{\bullet} \qquad k_3 = 2.2 \times 10^{10}\ M^{-1}\ s^{-1}\ {}^{16} \qquad (3)$$

$$OH^{\bullet}/H^{\bullet} + RH \rightarrow H_2O/H_2 + R^{\bullet} \qquad (4)$$

If the solutions also contain a metal ion (M^{n+}(aq)) and $[M^{n+}(aq)] <$ [RH], $[N_2O]$, then the aliphatic radical may react with the metal ion to form a transient with a metal–carbon σ-bond:

$$M^{n+}(aq) + R^{\bullet} \rightarrow [M^{n+1}–R]^{n+} \qquad (5)$$

At pH ≥3, e_{aq}^- and $OH^{\bullet}$ are converted into the aliphatic radical, whereas $H^{\bullet}$, which contributes about 10% to the total radical yield, may react with the metal ions, as in many cases k_4 for $H^{\bullet}$ is considerably lower than k_4 for $OH^{\bullet}$.[16] At pH <3, the contribution of $H^{\bullet}$ radicals to the total radical yield is more than 10% due to reaction 3 and the yield of $[M^{n+1}–R]^{n+}$ decreases with the increase of $[H^+]$.

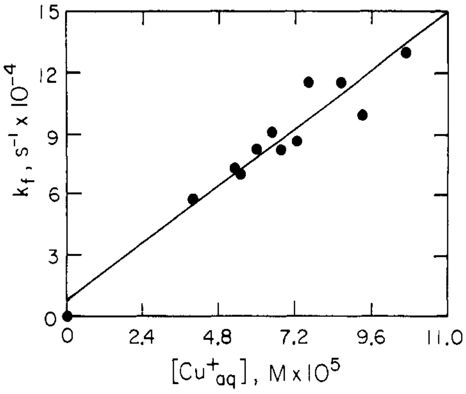

Figure 2. Observed rate constant for the formation of $[Cu^{II}–CH_2C(CH_3)_2(NH_3^+)]^+$ measured at 375 nm as a function of $[Cu^+(aq)]$. N_2O-saturated solutions contained 0.02–0.2 M 2-methyl-2-propanamine and 0–5 × 10^{-4} M $CuSO_4$ at pH 3.

Table I. Observed Rate Constants for Formation (k_f) and Decomposition (k_d) of $[Cu^{II}–CH_2C(CH_3)_2(NH_3^+)]^+$ in N_2O-Saturated Solutions under Various Conditions

$[Cu^+(aq)]$, M	$[Cu^{2+}(aq)]$, M	$[(CH_3)_3CNH_3^+]$, M	pH	k_f, s^{-1}	k_d, s^{-1}
3.9×10^{-5}	5×10^{-4}	0.1	3	5.8×10^4	5.6
5.2×10^{-5}	5×10^{-4}	0.1	5	7.0×10^4	5.7
6.5×10^{-5}		0.1	3	8.6×10^4	6.0
6.5×10^{-5}		0.1	1.5	9.2×10^4	6.3
6.5×10^{-5}	5×10^{-4}	0.1	3	8.3×10^4	6.2
6.5×10^{-5}	1×10^{-3}	0.1	3	9.2×10^4	6.6
6.5×10^{-5}	2×10^{-3}	0.1	3	1.1×10^5	7.6
6.5×10^{-5}	5×10^{-4}	0.02	3	8.3×10^4	7.1
6.5×10^{-5}	5×10^{-4}	0.2	3	1.1×10^5	8.3
6.5×10^{-5}	5×10^{-4}	0.2	3	1.1×10^5	8.3
8.5×10^{-5}		0.1	2	1.2×10^5	7.0
9.1×10^{-5}	5×10^{-4}	0.1	3	9.5×10^4	6.4
1.1×10^{-4}		0.1	3	1.3×10^5	7.4
9.1×10^{-5}	5×10^{-4}	0.1	3	1.1×10^5	7.4

Table II. Observed Rate Constants for Formation (k_f) and Decomposition (k_d) of $[(H_2O)_5Cr^{III}–CH_2C(CH_3)_2(NH_3^+)]^{2+}$ in N_2O-Saturated Solutions under Various Conditions

$[Cr(H_2O)_6^{2+}]$, M	$[(CH_3)_3CNH_3^+]$, M	pH	k_f, s^{-1}	k_d, s^{-1}
1×10^{-4}	0.09	3	2.0×10^3	0.015
2×10^{-4}	0.08	3	3.3×10^3	0.016
4×10^{-4}	0.09	3	1.1×10^4	0.012
8×10^{-4}	0.09	3	1.6×10^4	0.013
1×10^{-3}	0.09	3	2.2×10^4	0.015
1×10^{-3}	0.09	2	2.0×10^4	0.017
1×10^{-3}	0.09	1	2.6×10^3	0.014

Results

The Cu^+(aq)–2-Methyl-2-propanamine System. Nitrous oxide solutions containing 0.02–0.1 M 2-methyl-2-propanamine in the pH range 1.5–5 and at (0.3–1.1) × 10^{-4} M Cu^+(aq) were pulse-irradiated. Formation of a transient absorption was observed (Figure 1). The transient absorbs at 385 ± 5 nm with $\epsilon = 2500 \pm 300$ M^{-1} cm^{-1}. The rate of the formation of the transient obeys a pseudo-first-order law. The observed rate constant is linearly dependent on $[Cu^+(aq)]$ (Figure 2), slightly dependent on $[CuSO_4]$, and independent of [2-methyl-2-propanamine] and pH (Table I). From the slope of the line in Figure 2, a rate constant of (1.2 ± 0.2) × 10^9 M^{-1} s^{-1} is calculated. The rate of the decomposition of the transient obeys a first-order rate law and $k = 7.0 \pm 1.4$ s^{-1}, independent of [2-methyl-2-propanamine], $[Cu^+(aq)]$, $[CuSO_4]$, and pH (Table I). A typical kinetic plot is given in Figure 3a. The final gas products were analyzed by gas chromatography, and 2-methylpropene was found to be formed with a yield of $G(CH_2{=}C(CH_3)_2) = 5.4 \pm 0.5$.

The $Cr(H_2O)_6^{2+}$–2-Methyl-2-propanamine System. Nitrous oxide solutions containing 0.09 M 2-methyl-2-propanamine in the pH range 1–3 and at (0.1–1) × 10^{-3} M $Cr(H_2O)_6^{2+}$ were

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(15) Diel, H.; Frederick Smith, G.; Schilt, A. A.; McBride, L. The copper reagents: cuproine, neocuproine, and bathocuproine (G. Frederick Smith Chemical Co., Columbus, OH, 1972).

(16) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *117*, 513.

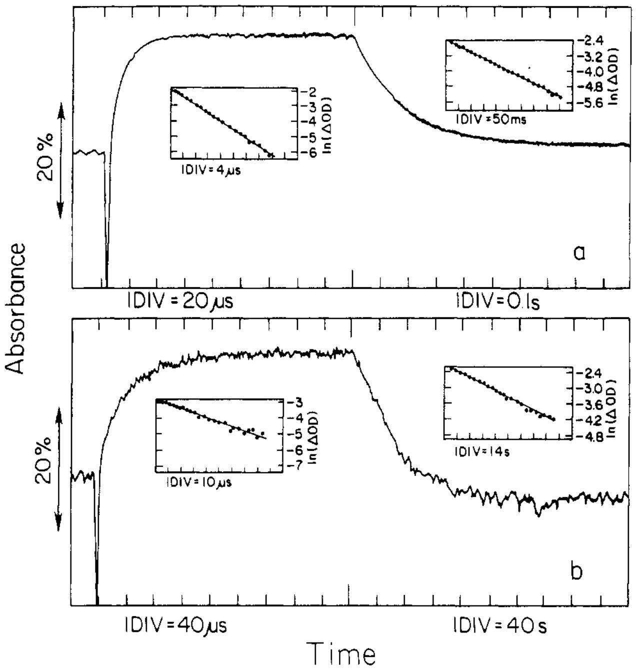

Figure 3. Kinetics plots obtained in pulse-irradiated N_2O-saturated solutions containing (a) 65 μM Cu^+(aq) and 0.1 M 2-methyl-2-propanamine at pH 3 ($\lambda = 375$ nm) and (b) 1 mM $Cr(H_2O)_6^{2+}$ and 0.09 M 2-methyl-2-propanamine at pH 2 ($\lambda = 285$ nm). The inset contains fits to first-order reactions. The optical path length was 12.1 cm, and the dose was 1 krad.

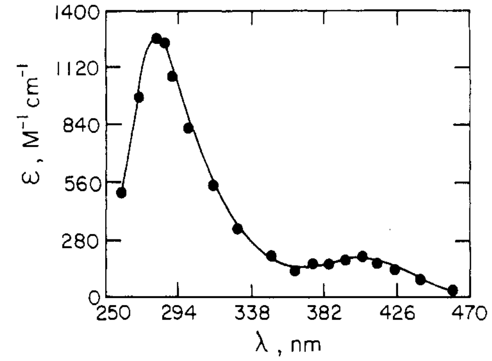

Figure 4. Absorption spectrum of $[(H_2O)_5Cr^{III}{-}CH_2C(CH_3)_2(NH_3^+)]^{2+}$ formed in a pulse-irradiated N_2O-saturated solution containing 1×10^{-3} M $Cr(H_2O)_6^{2+}$ and 0.09 M 2-methyl-2-propanamine at pH 3.

pulse-irradiated. Formation of a transient with a spectrum typical of chromium-substituted alkyl complexes was observed (Figure 4).[8] The rate of the formation of the transient is independent of the amine concentration and pH and is proportional to $[Cr(H_2O)_6^{2+}]$ (Table II, Figure 5). From the slope of the line in Figure 5, a rate constant of $(2.2 \pm 0.3) \times 10^7$ M^{-1} s^{-1} is calculated. The transient decomposes via a first-order reaction with a rate constant of 0.015 ± 0.003 s^{-1}, independent of [2-methyl-2-propanamine], $[Cr(H_2O)_6^{2+}]$, and pH (Table II). A typical kinetic plot is given in Figure 3b. We identified 2-methylpropene as one of the final products with $G(CH_2{=}C(CH_3)_2) = 5.3 \pm 0.2$.

The $Cr(H_2O)_6^{2+}$–2-Methyl-2-propanol System. Nitrous oxide solutions containing 0.18–0.47 M 2-methyl-2-propanol at pH 2–4 and (0.5–1) × 10^{-3} M $Cr(H_2O)_6^{2+}$ were pulse-irradiated. The spectrum of the transient formed and the rate of its formation are the same as has already been observed by Cohen and Meyerstein[8] under similar conditions. The rate of the formation of this transient could not be measured at pH ≤2 since the rate of the decay of the transient at low pH's approaches that of the formation, and there is an overlap between these two processes. However, the rates of the decomposition of this transient (Table III) exceed by three orders of magnitude at acid pH's those reported earlier.[8]

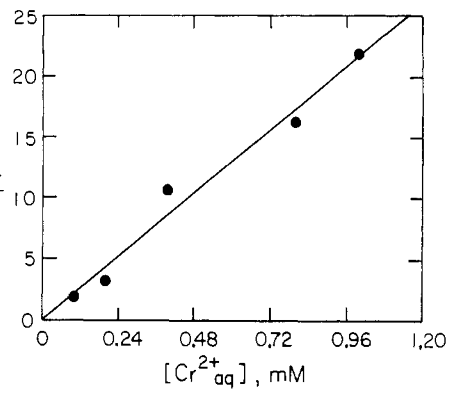

Figure 5. Observed rate constant for the formation of $[(H_2O)_5Cr^{III}{-}CH_2C(CH_3)_2(NH_3^+)]^{2+}$ measured at 285 nm vs $[Cr(H_2O)_6^{2+}]$. N_2O-saturated solutions contained 0.09 M 2-methyl-2-propanamine at pH 3.

Table III. Observed Rate Constants for Formation (k_f) and Decomposition (k_d) of $[(H_2O)_5Cr^{III}{-}CH_2C(CH_3)_2OH]^{2+}$ in N_2O-Saturated Solutions under Various Conditions

$[Cr(H_2O)_6^{2+}]$, M	$[(CH_3)_3COH]$, M	pH	k_f, s^{-1}	k_d, s^{-1}
5×10^{-4}	0.48	3	7.5×10^4	2.8×10^3
1×10^{-3}	0.45	3	1.1×10^5	2.4×10^3
1×10^{-3}	0.45	4	1.3×10^5	4.8×10^2
1×10^{-3}	0.45	2		2.7×10^4
1×10^{-3}	0.18	3	1.3×10^5	3.2×10^3
1×10^{-3}	0.18	2		2.8×10^4

Discussion

It has been demonstrated that at pH <10.5 there is only one radical formed via H abstraction from 2-methyl-2-propanamine[17]

$$OH^\bullet/H^\bullet + (CH_3)_3CNH_3^+ \rightarrow H_2O/H_2 + {}^\bullet CH_2C(CH_3)_2NH_3^+$$
$$k_{OH} = 7 \times 10^8\ M^{-1}\ s^{-1}\ {}^{17}\quad (k_H \text{ not determined}) \qquad (4a)$$

and the radical $(CH_3)_3C\dot{N}H$ is formed only at pH >11.[17] In the case of 2-methyl-2-propanol, mainly reaction 4b occurs, and the $(CH_3)_3CO^\bullet$ yield is only 4.3% under all conditions.[16]

$$OH^\bullet/H^\bullet + (CH_3)_3COH \rightarrow H_2O/H_2 + {}^\bullet CH_2C(CH_3)_2OH$$
$$k_{OH} = 6 \times 10^8\ M^{-1}\ s^{-1};^{16}\ k_H = 1.7 \times 10^5\ M^{-1}\ s^{-1}\ {}^{16} \qquad (4b)$$

When Cu^+(aq) was added to N_2O-saturated solutions containing 2-methyl-2-propanamine, the formation of a transient was observed with a spectrum similar to those of many other complexes with a Cu^{II}–carbon σ-bond.[5,7,18-21] Moreover, the observed rate constant of the formation of this transient depended linearly on $[Cu^+(aq)]$ (Figure 2), and therefore it is suggested that $[Cu^{II}{-}CH_2C(CH_3)_2(NH_3^+)]^+$ has been formed via reaction 5a. From

$$Cu^+(aq) + {}^\bullet CH_2C(CH_3)_2NH_3^+ \rightarrow [Cu^{II}{-}CH_2C(CH_3)_2(NH_3^+)]^+ \qquad (5a)$$

the slope of the line in Figure 2, $k_{5a} = (1.2 \pm 1.0) \times 10^9$ M^{-1} s^{-1} is calculated. This value is similar to those reported for other analogous reactions of Cu^+(aq) with aliphatic radicals.[3,5-8,18-21] It is about 4 times lower than that determined for the reaction of cuprous ions with ${}^\bullet CH_2C(CH_3)_2OH$ ($(4.5 \pm 1.0) \times 10^9$ M^{-1} s^{-1}),[7] which may be due to the positive charge of the free radical in the case of the amine. The addition of $CuSO_4$ to this system

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(17) Simic, M.; Neta, P.; Hayon, E. *Int. J. Radiat. Phys. Chem.* **1971**, *3*, 309.

(18) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1986**, *25*, 1505.

(19) Das, S.; Johnson, J. R. *J. Chem. Soc., Faraday Trans. 1* **1980**, *74*, 1779.

(20) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1987**, *26*, 2342.

(21) Masarwa, M.; Cohen, H.; Saar, J.; Meyerstein, D. *Isr. J. Chem.* **1990**, *30*, 361.

caused a slight increase in the rate of the formation only at concentrations exceeding 5×10^{-4} M (Table I). From the difference in the observed rate constant in the absence and in the presence of $Cu^{2+}(aq)$, a value of 1.4×10^7 M^{-1} s^{-1} was estimated for the reaction of cupric ions with the radical derived from 2-methyl-2-propanamine. This value is 2 orders of magnitude lower than the rate constant of the same radical with $Cu^+(aq)$ and is in accord with the relative rates of reactions of other aliphatic free radicals with cuprous and cupric ions.[3,5-7,18-21]

The kinetics of the decomposition of this transient obeyed a first-order rate law. The rate was independent of $[Cu^+(aq)]$, $[Cu^{2+}(aq)]$, [2-methyl-2-propanamine], and pH (Table I). 2-Methylpropene was found to be one of the final products of this process with a yield similar to that of the aliphatic free radical formed initially. Therefore, it follows that the observed decomposition reaction is the β elimination of ammonia via

$$[\mathrm{Cu^{II}{-}CH_2C(CH_3)_2(NH_3^+)}]^+ \rightarrow \mathrm{Cu^{2+}(aq) + CH_2{=}C(CH_3)_2 + NH_3} \quad (6)$$

In the case of 2-methyl-2-propanol, it was found[7] that the observed rate constant of the decomposition (k_d) of $[\mathrm{Cu^{II}{-}CH_2C(CH_3)_2OH}]^+$ was linearly dependent on $[H^+]$, obeying eq 7, where $k_0 = 5.0 \times 10^4$ s^{-1} and $k_{H^+} = 8.6 \times 10^7$ M^{-1} s^{-1}.

$$k_d = k_0 + k_{H^+}[H^+] \quad (7)$$

In the case where $Cr(H_2O)_6^{2+}$ was added to N_2O-saturated solutions containing 2-methyl-2-propanamine, the formation of a transient with a typical spectrum of complexes with a Cr^{III}–carbon σ-bond was observed (Figure 4).[8] The observed rate constant of the formation of this transient depends linearly on $[Cr(H_2O)_6^{2+}]$ (Figure 5), and therefore it follows that the transient is formed via

$$\mathrm{Cr(H_2O)_6^{2+} + {}^\bullet CH_2C(CH_3)_2NH_3^+} \rightarrow [\mathrm{(H_2O)_5Cr^{III}{-}CH_2C(CH_3)_2(NH_3^+)}]^{2+} \quad (5b)$$

where $k_{5b} = (2.2 \pm 0.3) \times 10^7$ M^{-1} s^{-1} (Figure 5). As in the case of the cuprous ions, this value is about 5 times lower than that obtained for the reaction of chromium ions with $^\bullet CH_2C(CH_3)_2OH$, which is $(1.1 \pm 0.1) \times 10^8$ M^{-1} s^{-1} (Table III and ref 8).

The results in the literature as well as those obtained in this study demonstrate that the specific rate constant of the formation of $[M^{n+1}{-}R]^{n+}$ is always lower in the case of $Cr(H_2O)_6^{2+}$ as compared to $Cu^+(aq)$ for the same aliphatic free radical. This observation might be due to the lower steric hindrance to the approach of the aliphatic radical to $Cu^+(aq)$ in comparison to $Cr(H_2O)_6^{2+}$.

It is worthwhile to note that the yield of $[M^{n+1}{-}R]^{n+}$ was pH independent in the 2-methyl-2-propanamine system. In the 2-methyl-2-propanol system, it decreased at pH 2 to about half the value obtained at pH ≥3. Therefore, we have to assume that the rate constant of the reaction of $H^\bullet$ with the amine is at least 2 orders of magnitude higher than that for the reaction with the alcohol. We have no explanation for this difference.

The kinetics of the decomposition of $[\mathrm{(H_2O)_5Cr^{III}{-}CH_2C(CH_3)_2(NH_3^+)}]^{2+}$ obeyed a first-order rate law independent of $[Cr(H_2O)_6^{2+}]$, [2-methyl-2-propanamine], and pH. Moreover, it was found that 2-methylpropene is one of the final products of this process and its yield is within experimental error the same as that of the aliphatic free radical formed initially. It follows therefore that the observed decomposition reaction is described by

$$[\mathrm{(H_2O)_5Cr^{III}{-}CH_2C(CH_3)_2(NH_3^+)}]^{2+} \rightarrow \mathrm{Cr^{3+}(aq) + CH_2{=}C(CH_3)_2 + NH_3} \quad (8)$$

In the case of $[\mathrm{(H_2O)_5Cr^{III}{-}CH_2C(CH_3)_2OH}]^{2+}$ it was found from the data present in Table III that the rate constant of the decomposition of this transient obeyed eq 7, where $k_0 = 160$ s^{-1} and $k_{H^+} = 2.7 \times 10^6$ M^{-1} s^{-1}. The acid-catalyzed term is about 3 orders of magnitude higher than that reported earlier by Cohen and Meyerstein.[8] (The source of the error in the original paper is unclear.)

Table IV. Rates of β-Elimination Reactions

RH	$M^{n+}(aq)$	k_0, s^{-1}	k_{H^+}, M^{-1} s^{-1}
$(CH_3)_3COH$	$Cu^+(aq)$	5×10^4	8.6×10^7
$(CH_3)_3COH$	$Cr(H_2O)_6^{2+}$	1.6×10^2	2.7×10^6
$(CH_3)_3CNH_3^+$	$Cu^+(aq)$	7.0	
$(CH_3)_3CNH_3^+$	$Cr(H_2O)_6^{2+}$	0.015	

The mechanism of the loss of ammonia from $[\mathrm{M^{n+1}{-}CH_2C(CH_3)_2(NH_3^+)}]^{n+}$ is described by reactions 6 and 8. The amine is always protonated under our experimental conditions, and therefore these transients lose ammonia directly via a β-elimination process with pH-independent rates.

The rate of the β-hydroxyl elimination processes for a large variety of $[\mathrm{L_mM^{n+1}{-}CR^1R^2CR^3R^4OH}]^{n+}$ complexes obeys eq 7.[5-11,22] In some cases the acid-noncatalyzed route (k_0) is the major process observed whereas in others, such as the present system, the acid-catalyzed process is the major one.

The acid-catalyzed process is believed to proceed via the reactions

$$[\mathrm{M^{n+1}{-}CH_2C(CH_3)_2OH}]^{n+} + \mathrm{H^+} \rightleftharpoons [\mathrm{M^{n+1}{-}CH_2C(CH_3)_2(OH_2^+)}]^{n+} \quad (9)$$

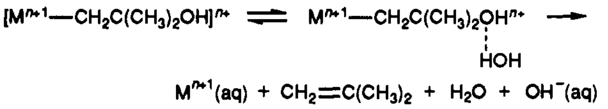
$$[\mathrm{M^{n+1}{-}CH_2C(CH_3)_2(OH_2^+)}]^{n+} \rightarrow \mathrm{M^{n+1}(aq) + CH_2{=}C(CH_3)_2 + H_2O} \quad (10)$$

where reaction 9 is a fast equilibrium process. The observed rate constant for the decomposition process obtained from these reactions is

$$k_d = K_9k_{10}[H^+]/(1 + K_9[H^+])$$

Thus, the observed rate constant of the acid-catalyzed path, k_{H^+}, equals K_9k_{10}. Therefore, k_6 and k_8 should be compared with k_{10} and not with k_{H^+}. However, as k_6, $k_8 \ll k_{H^+}$ and as $K_9 \ll 1$, clearly k_6, $k_8 \ll k_{10}$.

The detailed mechanism of the acid-noncatalyzed reaction is not clear. It is generally believed that the reaction occurring is the elimination of a hydroxide ion.[7-11,22] However, it is plausible that the reaction observed is a proton transfer from a water molecule to the hydroxyl followed by the elimination of a water molecule,[23] i.e., reaction 11. For simplicity in the following we assume that a hydroxide is eliminated. This assumption does not affect the conclusions.



$$[\mathrm{M^{n+1}{-}CH_2C(CH_3)_2OH}]^{n+} \rightleftharpoons \mathrm{M^{n+1}{-}CH_2C(CH_3)_2\underset{\substack{\vdots\\ HOH}}{O}H^{n+}} \rightarrow \mathrm{M^{n+1}(aq) + CH_2{=}C(CH_3)_2 + H_2O + OH^-(aq)} \quad (11)$$

The rates of the β-elimination reactions discussed are summarized in Table IV. From this table it is evident that the β elimination of the NH_3 group is many orders of magnitude slower than that of the H_2O group, i.e., than that of the acid-catalyzed β-hydroxyl elimination. Moreover, the observed rates are even slower than those of the corresponding acid-independent β-hydroxyl eliminations. The source of this observation is analyzed in detail below.

Why Does β Elimination of Ammonia Proceed More Slowly Than β Elimination of Water? A Valence-Bond Rationale

The rate-determining step of the β elimination involves presumably C–N and C–O bond cleavages. Since the former bond is normally weaker than the latter,[4] it is quite puzzling to find that the β elimination of NH_3 is much slower than that of H_2O. This section offers a rationale of the trend based on a valence bond (VB) consideration of bond strengths.[24]

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(22) Cohen, H.; Ish-Shalom, R.; Feldman, A.; Meyerstein, D. *J. Am. Chem. Soc.* **1991**, *113*, 5292.

(23) We thank the reviewer for raising this possibility.

(24) (a) Maitre, P.; Lefour, J. M.; Ohanessian, G.; Hiberty, P. C. *J. Phys. Chem.* **1990**, *94*, 4082. (b) Sini, G.; Maitre, P.; Hiberty, P. C.; Shaik, S. S. *THEOCHEM* **1991**, *229*, 163.

Table V. Bond Energy Data for R–X and R–XH$^+$ Species

entry	R–X	*D*(R–X),[a] kcal/mol	*D*(R–XH$^+$), kcal/mol
1	CH_3–OH	91; (92.3 ± 1.0)	68.5[b]
2	CH_3–NH_2	80; (84.9 ± 1.1)	105.2[b]
3	C_2H_5–OH	91	37.0[c]
4	C_2H_5–NH_2	78	72.0[c]
5	$(CH_3)_2CH$–OH	92	22.8[c]
6	$(CH_3)_2CH$–NH_2	79	52.0[c]
7	$(CH_3)_3C$–OH	91	11.2[b,c]
8	$(CH_3)_3C$–NH_2	77	39.0;[b] 40.0[c]

[a] In entries 1 and 2, the parenthetical data are from ref 4a. The rest of the data are from ref 4b. [b] From ref 25a. These are R$^+$ affinity values (eq 12). [c] From ref 25b. These are R$^+$ affinity values (eq 12).

Let us first review some bonding data[4,25] displayed in Table V. The *D*(R–XH$^+$) values refer to alkyl cation affinities according to eq 12, as discussed by Meot-Ner et al.[25a] and by Kebarle et al.,[25b] while *D*(R–X) refers to the usual homolytic bond energies. As will be shown immediately, there exists a good basis to compare these two quantities, *D*(R–XH$^+$) and *D*(R–X).

$$R\text{–}XH^+ \rightarrow R^+ + XH;\quad X = NH_2, OH \qquad (12)$$

A few important trends are apparent in the table. First, in all the unprotonated species the relationship *D*(C–O) > *D*(C–N) holds consistently, irrespective of the nature of the alkyl group. Second, upon protonation *there occurs an inversion* in the relative strength, which becomes now *D*(C–N) > *D*(C–O). This inversion occurs generally due to a more substantial C–O bonding interaction weakening by heteroatom protonation. It is apparent also, as noted by Meot-Ner et al.,[25a] that the weakening accelerates as the R$^+$ group becomes a more stabilized carbonium ion. Thus, in the case of 2-methyl-2-propanol the C–OH_2^+ bond is best described as a loosely solvated carbonium ion, $(CH_3)C^+\cdots OH_2$.[25b] The respective C–NH_3^+ bond is still significantly strong, with *D*(R–XH$^+$) = 40 kcal/mol. In one case in Table V, that of *R* = CH_3, the protonation has a spectacular effect on the bond energies. Thus, CH_3–NH_3^+ is a much stronger bond than its nonprotonated analogue, CH_3–NH_2, while the corresponding C–O bond behaves normally and is weakened by protonation. We emphasize at this point that there is a good basis to compare the methyl cation affinity value, *D*(CH_3–NH_3^+), to the corresponding homolytic bond strength, *D*(CH_3–NH_2). This is so because in both cases *we are comparing the bonded species to its fragments of their electronic configurations of the lowest energy*. Otherwise, there would be of course little point in comparing heterolytic and homolytic bond energies. The following discussion refers only to those cases where the comparison of *D*(R–XH$^+$) and *D*(R–X) is proper.

It appears therefore from Table V that protonation reverses the bond strength order of the C–N and the C–O bonds. This in itself is sufficient to rationalize our experimental findings that β elimination of NH_3 is slower than β elimination of H_2O.

While the root cause for the puzzling kinetic results is now more lucid, there remains the need to understand the nature of the bond strength modulation by protonation. For this purpose we use VB ideas coupled with some ab-initio SCF-MO computations of protonated R–OH and R–NH_2 molecules.

Consider the unprotonated R–X bonds. According to VB ideas, an electron-pair bond of this type can be described as a result of the mixing of a covalent form R$^\bullet$–$^\bullet$X and an ionic form R$^+$:X$^-$.[26] The lower energy form is R$^\bullet$–$^\bullet$X and part of the bond energy is contributed by the spin-pairing in the covalent form. This covalent contribution may be estimated using one of the averaging formulas of Pauling,[4b,24b,26] e.g. (13), where *m* is a correction factor.[4b]

$$D_{cov}(R\text{–}X) \simeq m[D(R\text{–}R)\ D(X\text{–}X)]^{1/2} \qquad (13)$$

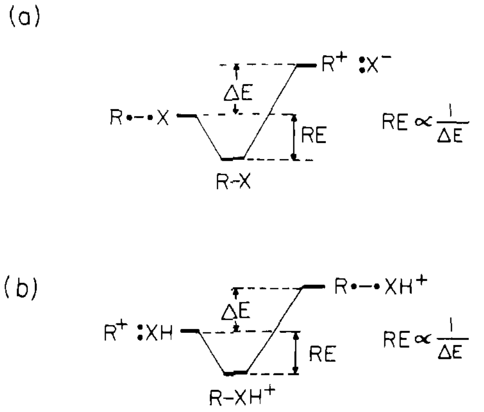

Figure 6. VB mixing diagrams[25] for R–X and R–XH$^+$ bonds.

Using appropriate bond energy data,[4b] we find that this covalent contribution is 71 kcal/mol for C–O and 73 kcal/mol for C–N. The remainder of the bond energy is contributed by the resonance energy (RE) due to the mixing of R$^\bullet$–$^\bullet$X with R$^+$:X$^-$, as shown schematically in the VB mixing diagram in Figure 6a.[24b,27] It is here where the distinction between the two bonds comes to the fore. Using simple perturbation theoretic arguments,[27] the RE will be *inversely proportional* to the energy gap Δ*E* between the two VB forms. Since the electron affinity of OH is larger than that of NH_2 by approximately 25 kcal/mol,[28] the C–OH bond will possess higher RE and be stronger and more polar than C–NH_2, as is indeed apparent in Table V.

Protonation of the heteroatom has a tremendous impact on the energy of the configurations and on their mixing, as shown in Figure 6b. The covalent form is now destabilized, primarily because as a protonated form it has to be generated by *one electron shift* from the neutral XH (XH = NH_3, OH_2) molecule to R$^+$, and this is more costly and overrides the spin-pairing interaction in the covalent form.[29,30] The most stable VB form is then the carbocationic structure, R$^+$:XH. This form is slightly bound by ion–dipole type interactions, which may be of the order of ≤20 kcal/mol.[31] The rest of the bonding must result therefore from the charge-shift RE due to the mixing of the two VB forms. This can be discussed by appeal to the perturbation theoretic argument which relates RE to the inverse of the energy gap (Δ*E*) between the VB configurations. This energy gap is governed by the ionization potential difference IP(XH) – IF(R$^\bullet$).

Consider first a series with the same XH and a varying R group. As R$^+$ becomes more stable, the gap increases because IP(R$^\bullet$) decreases, and the RE stabilization diminishes. This is indeed what Table V shows, and one may see that for $(CH_3)_3COH_2^+$ the bond energy is extremely small and very likely most of the bonding is due to ion–dipole interaction in the $(CH_3)_3C^+\cdots OH_2$ VB form. These conclusions are in harmony with the recent analysis of Meot-Ner et al.[25a]

Consider now a comparison between R–OH_2^+ and R–NH_3^+. Since R is identical, what will determine the energy gap for VB mixing is IP(H_2O) in comparison with IP(NH_3). Since the former

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(25) (a) Meot-Ner, M.; Karpas, Z.; Deakyne, C. A. *J. Am. Chem. Soc.* **1986**, *108*, 3913. (b) Hiraoka, K.; Kebarle, P. *J. Am. Chem. Soc.* **1977**, *99*, 360.

(26) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1939.

(27) Shaik, S. S. In *New Theoretical Concepts for Understanding Chemical Reactions*; NATO ASI Series, Vol. C267; Bertran, J., Csizmadia, I. G., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989.

(28) Hiraoka, K.; Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1973**, *95*, 1833.

(29) *D*(HX–XH^{2+}) is negative, and therefore only the arithmetic sum formula can be used in eq 12, which becomes D_{cov}(R–XH$^+$) = 0.5*m*[*D*(R–R) + (*D*(HX–XH^{2+})]. Using *D*(HX–XH^{2+}) data from ref 28, we obtain the following values: D_{cov}(R–OH_2^+) = –7.5 kcal/mol; D_{cov}(R–NH_3^+) = 16 kcal/mol.

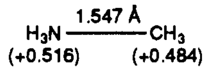
(30) Gill, P. M. W.; Radom, L. *J. Am. Chem. Soc.* **1989**, *111*, 4613.

(31) See for example experimental data on cation–molecule interactions in: (a) Davidson, W. R.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 6125. (b) Meot-Ner, M.; Samy El-Shall, M. *J. Am. Chem. Soc.* **1986**, *108*, 4386. Theoretical data are also in line with this estimate of ion–dipole type energies. See, e.g.: Williams, I. H. *J. Am. Chem. Soc.* **1984**, *106*, 7206 (for NH_3 interacting with $CH_3NH_3^+$). Raghavachari, K.; Chandrasekhar, J.; Burnier, R. C. *J. Am. Chem. Soc.* **1984**, *106*, 3124 (for the interaction of H_2O with CH_3OH^{2+}).

is 40 kcal/mol larger than the latter,[32] the gap for VB mixing will accordingly be larger for R–OH_2^+. It follows therefore that all R–OH_2^+ bonds will have smaller RE's than the corresponding R–NH_3^+. This is the root cause for ***the reversal in the strengths of the R–O vs R–N bonds*** upon protonation as displayed by the data in Table V. We may therefore conclude that the fundamental reason for the slower β elimination of NH_3 relative to H_2O is the more intense charge-shift resonance, which is obtained from the mixing of the R–NH_3^+ form with the R^+:NH_3 form in comparison with the (R–OH_2)$^+$ analogues.

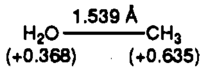
Turning back to Figure 6b, we may attempt to elucidate a few more trends. According to the model, the protonation destabilizes the covalent form[29] and the R–XH^+ bond loses the major part of its spin-pairing energy. The resulting bond is sustained by a combination of the ion–dipole interaction and the charge-shift resonance energy stabilization. This is the origin of the bond weakening that is caused by protonation as displayed in Table V.

There is, however, one exception in Table V, and this is the CH_3–NH_3^+ bond, which is strengthened by as much as 20 kcal/mol upon protonation. The VB in Figure 6b allows us to rationalize this spectacular effect in a quite lucid manner. Thus, when the two VB forms become degenerate or nearly so, the RE is maximized and fully manifested in the bond energy. If such a case occurs, it may well be that the protonated bond, being sustained by a large RE, would also be stronger than the unprotonated bond. We recall that the energy gap between the configurations is governed by the ionization potential difference IP(XH) − IP(R$^\bullet$). When R is CH_3 the IP($^\bullet CH_3$) is a large value of 227 kcal/mol, very close to the ionization potential of NH_3.[32] This together with some spin-pairing stabilization[29] of the VB form $H_3C^\bullet$–$^\bullet NH_3^+$ brings the two configurations into degeneracy. That this is approximately so can be judged from the Mulliken group charges of the CH_3–NH_3^+ species computed by the 3-21G basis set[33] in I. In II we show the corresponding Mulliken charges for CH_3–OH_2^+.



$\underset{(+0.516)}{H_3N}\overset{1.547\ \text{Å}}{\text{———}}\underset{(+0.484)}{CH_3}$

I

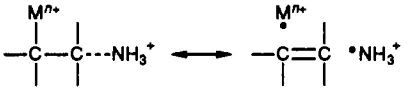


$\underset{(+0.368)}{H_2O}\overset{1.539\ \text{Å}}{\text{———}}\underset{(+0.635)}{CH_3}$

II

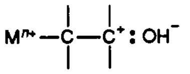
The approximately equal group charges in CH_3–NH_3^+ indicate that the VB configurations are near degeneracy in comparison with CH_3–OH_2^+, where the lowest and major configuration of the bond remains the form CH_3^+:OH_2. We believe that this is the main reason that the CH_3–N bond is strengthened while the CH_3–O bond is weakened by protonation. Thus, CH_3–NH_3^+ is a unique "resonating σ-bond"[24b] *in which the charge-shift resonance is fully manifested in the bonding*. In general, because IP(NH_3) < IP(H_2O), there will exist better chances to encounter charge-shift-resonating R–NH_3^+ bonds, which experience bond strengthening upon protonation. This is less likely for R–OH_2^+ bonds, owing to the high IP(H_2O).

What can be said about ($M^{n+1}CH_2C(CH_3)_2$–NH_3^+)$^{n+}$(aq)? If this bond is like $(CH_3)_3C$–NH_3^+, then it is not apparent why should this complex β-eliminate *more slowly* than ($M^{n+1}CH_2C(CH_3)_2$–OH)$^{n+}$(aq). There exists a possibility that the metal assists the C–OH bond breaking by insertion into this bond. While we cannot rule out this mechanism, we must also consider an alternative which is in line with our VB explanation. This alternative mechanism is that the metal ion may endow the C–NH_3^+ bond with a charge-shift-resonating nature. It might then be expected that, much like the case of the free C–NH_3^+ situation, in the complex, too, the C–NH_3^+ bond will be stronger than both C–OH_2^+ and C–OH. Some possible effects in this direction are the electron-withdrawing nature of M^{n+}, which raises the IP(R$^\bullet$) of the $M^{n+}CH_2\dot{C}(CH_3)_2$ moiety and at the same time stabilizes the covalent form of the bond by allowing spin-coupling with the M–C bond as shown in III. These two effects together may decrease



III

the VB mixing gap and push the bond in the "resonating" direction. One may also make a point in favor of the C–OH bond weakening in the complex due to the destabilization of the ionic form



M^{n+}—C—C^+: OH^-

A combination of these effects may then render the C–NH_3^+ bond stronger than the C–OH bond and provide a rationale for the corresponding ease of the latter bond to β-eliminate. Thus, while we are not enamored with our explanation, we feel that it provides a basis for future investigation of the problem.

Conclusions

The results obtained in this study indicate that the rate of the β elimination of X^- from $[M^{n+1}$–$CH_2C(CH_3)_2X]^{n+}$ is considerably slower for X = NH_3^+ than for X = OH or H_2O^+. A theoretical analysis suggests that the rates of these β-elimination reactions are correlated to the C–X bond strengths. Thus, the results indicate that the metal center exerts a large inductive effect, which affects considerably the C–X bond strength; i.e., though the C–X bond strength is larger in $(CH_3)_3COH$ than in $(CH_3)_3CNH_3^+$, the reverse seems to be true for the $[M^{n+1}$–$CH_2C(CH_3)_2X]^{n+}$ complexes. This conclusion is in accord with the large effect of L_mCo^{III}– on the pK_a of the hydroxyl group in $[L_mCo^{III}CR^1R^2OH]^{2+}$.[34]

Such an inductive effect might affect considerably the chemical properties of complexes with metal–carbon σ-bonds. We plan therefore to extend our studies in order to verify the existence of this effect and to analyze the factors which affect its magnitude.

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Registry No. $Cu(CH_3CN)_4PF_6$, 64443-05-6; Cu^+, 17493-86-6; $Cr(H_2O)_6^{2+}$, 20574-26-9; $^\bullet CH_2C(CH_3)_2OH$, 5723-74-0; $^\bullet CH_2C(CH_3)_2NH_3^+$, 114377-24-1; $OH^\bullet$, 3352-57-6; $H^\bullet$, 12385-13-6; H_2, 9116-20-5; $[(H_2O)_5Cr^{III}$–$CH_2C(CH_3)_2(NH_3^+)]^{2+}$, 138259-49-1; $[(H_2O)_5Cr^{III}$–$CH_2C(CH_3)_2OH]^{2+}$, 51965-50-5; $CH_3NH_3^+$, 17000-00-9; $CH_3OH_2^+$, 17836-08-7; chromium(II) perchlorate, 13931-95-8; 2-methyl-2-propanamine, 75-64-9; 2-methyl-2-propanol, 75-65-0.

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[32] Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 9.

[33] We used the GAUSSIAN 86 package by M. J. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, R. Melius, L. Martin, J. J. P. Stewart, F. W. Babrowicz, C. M. Rohlfing, L. R. Kahn, D. J. De-Frees, R. Seeger, R. A. Whiteside, D. J. Fox, E. M. Fleuder, and J. A. Pople, Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA, 1984.

[34] Meyerstein, D.; Schwarz, H. A. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 2933.