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Reactions of Cr^+ and Mn^+ with Propane and Propene in a Spark Plasma

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In reactions of first-row transition metal ions with hydrocarbons the formation of the metal ion–methyl bond in MCH_3^+ proceeds through a metal–ion configuration containing a $4s^1$ electron [1]. Consequently the $CrCH_3^+$ ion is not formed in mixtures of ground-state Cr^+ and small hydrocarbons, for Cr^+ has the stable $3d^5$ ground state. This restriction is not the only one, however. Although Mn^+ has the $3d^54s^1$ ground state, $MnCH_3^+$ is not observed among the products of mixture of small hydrocarbons and Mn^+. The explanation offered is that **two** metal-carbon bonds are formed in the intermediate (equation 1), and that while Mn^+ has a 4s electron to form the first, formation of the second is prevented because the stability of the remaining d^5 configuration prevents promotion of another electron to the s state needed to form the second bond [1].

$$M^+ + R{-}R \longrightarrow [R{-}M{-}R^+]^* \longrightarrow RM^+ + R^\cdot \qquad (1)$$

The reactivities of Cu^+, Ag^+, and Au^+ formed in a spark depend strongly on the energy levels of the lower excited states of the ions [2, 3]. The proposed intervention of excited states of these ions in ion–molecule reactions after sparking led to the proposal to demonstrate excited-state reactivity unobserved in the ground state processes of Cr^+ and Mn^+. We have indeed found that Cr^+ and Mn^+ generated in a spark source mass spectrometer react with propane and propene, and thus supply chemical evidence for the existence and adequate lifetime of excited states of these ions.

Experimental

The Cr^+ and Mn^+ ions were generated in an MS702 spark source mass spectrometer using electrodes formed by mixing $CrCl_3$ or Mn_3O_4 with graphite. Propane or propene was admitted at a pressure of 7×10^{-5} torr. The spark voltage was 30 kV; the pulse length was 100 μsec; the pulse repetition rate was 1000 Hz; plates were exposed until 20 nC Mn^+ or 25 nC Cr^+ ions were passed.

Results and Discussion

In propane $CrCH_3^+$ accounts for 44% of the total organometallic products observed, and $MnCH_3^+$ for 38%, with propane. The corresponding figures are 32% and 23% for propene. The remainder of the spectrum is divided between other one- and two-carbon organometallic species formed by further decomposition of alkylmetal ions. The intensity of the MCH_3^+ ions in each spectrum may then be taken as a guide to the reactivity of sufficiently long-lived lower excited states.

The energy distribution of heavy species immediately after sparking is not thermal [4], but 1 μsec after sparking it corresponds roughly to 1×10^4 K [5]. At this temperature the mean kinetic energy of a particle is 2.5 eV. The lowest $4s^1$ states of Mn^+ include the ^5G states beginning at 3.41 eV, the ^5P at 3.70 eV, and the ^5D at 4.06 eV, all of multiplicity different from the ground ^7S and therefore likely to be of appropriate lifetime. Similarly, the lower $4s^1$ states of Cr^+ include the ^4D states beginning at 2.42 eV, the ^4H at 3.74 eV, the ^4F at 3.85 eV, the ^2H at 4.29 eV, and the ^2P at 4.30 eV, all sufficiently accessible under these conditions and long-lived (the ground state of Cr^+ is ^6S) [6]. The formation of substantial fractions of excited state ions from vaporized metal is thus to be expected, and their lifetimes should be adequate to produce excited-state ion-molecule reactions.

The reaction of an electrode metal and organic vapor to give organometallic ions occurs through the reaction of the metal ion and the neutral organic molecule [2]. The reaction of the organic ion and the metal atom accounts for less than 0.01% of organometallic products. The fraction of organometallic products formed by reaction of metal ion and organic radicals formed in the spark is limited by the fraction of neutral molecules in the source region cleaved to radicals by the spark. (The path length and velocity of charged species are sufficient to make virtually the entire volume of the source housing accessible to metal ion energized by sparking. The collision rate constant between metal and radical is of the same order of magnitude as the collision rate constant between metal ion and parent neutral molecule).

Excited states of Cr^+ have been observed to react with alkanes previously [7, 8], but the observation of the reactivity of Mn^+ formed directly from the metal is novel. Observation of organometallic product ions demands that the excited states of the metals able to form sigma bonds intervene, since the ground states are incapable [1] of forming them. Since the fraction of MCH_3^+ is substantial, the population of the metal-ion state capable of forming these products is large, as expected from the energy levels of

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appropriate states and the temperature of species in the spark. The spark source experiment has, of course, no energy resolution, and does not indicate to what extent each quintet state of Mn^+ and each quartet or doublet state of Cr^+ is responsible for bond formation.

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