

(m, 10 H, (CH<sub>2</sub>)<sub>5</sub>); 2.08 (s, 2 H, NH<sub>2</sub>); 2.52, 2.98 (d.d, 2 H, H<sub>A</sub>, H<sub>B</sub>, *J* = 18.5 Hz).

**4-Amino-1,1,1-trifluoro-5-hydroxy-5,5-pentamethylene-pent-3-en-2-one (3).** M.p. 127–128 °C. Found (%): C, 50.70; H, 5.91; N 5.92. C<sub>10</sub>H<sub>14</sub>F<sub>3</sub>NO<sub>2</sub>. Calculated (%): C, 50.63; H, 5.95; N, 5.90. IR (Vaseline oil),  $\nu/\text{cm}^{-1}$ : 3410, 3310, 3210 (OH, NH<sub>2</sub>); 1605, 1530 (NH<sub>2</sub>, C=C–C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 1.69 (m, 10 H, (CH<sub>2</sub>)<sub>5</sub>); 2.14 (s, 1 H, OH); 5.39 (d, 1 H, =CH, *J* = 1.6 Hz); 7.4, 10.4 (br.s, 2 H, NH<sub>2</sub>).

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Received March 22, 1996;  
in revised form April 17, 1996

## Reactions of fullerenes with deuterium in the presence of palladium

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It has been reported<sup>1</sup> that fullerene deuteride C<sub>60</sub>D<sub>x</sub> has been obtained as the result of the reaction between gaseous deuterium and palladium fulleride under rather mild conditions (473 K, 2 MPa). Mass spectrometric analysis of the obtained deuteride C<sub>60</sub>D<sub>x</sub> showed that *x* varies from 2 to >30 with local maxima at 2, 4, 18, and 26. It was also mentioned that palladium clusterization took place during the reaction. These observations gave reason to believe that palladium clusters take an active part in the gas phase deuteration of fullerenes.

In this work, we report the results of an investigation of the reaction of D<sub>2</sub> with fullerite (78 % C<sub>60</sub> + 22 % C<sub>70</sub>) in the presence of palladium clusters (Pd/C catalyst, specific surface of the carrier ~350 m<sup>2</sup>/g, Pd content 10 wt. %) as well as of palladium metallic powder (average size of the particles was ~10 nm.)

A homogeneous mixture of Pd or Pd/C (50 wt. %) + Ful (50 wt. %), where Ful is fullerite, was obtained by stirring in a vibration mill (amplitude 10 mm, ball load 50 : 1, argon medium, time 30 min.). Degasification of the mixture was carried out before deuteration by heating up to 500 K *in vacuo* (~1 Pa). Deuterium was injected after the sample had cooled down to 300 K. Deuteration was carried out at pressures from 1.0 to 2.5 MPa and

temperatures from 473 K to 673 K. The reaction products were removed from an autoclave in an inert atmosphere after they had cooled to room temperature.

An *endo*-effect followed by liberation of ~1 wt. % of gas, which corresponds to deuterium liberation from palladium deuteride of the composition of PdD<sub>0.9</sub>, can be seen on the thermogravigram of deuterated mixtures of Pd + Ful at 373 to 400 K in an argon atmosphere. A second *endo*-effect with gas liberation can be clearly seen at ~800 K. Depending on the conditions of the deuteration of the initial mixture, the weight loss was from 0 (473 K, 1 MPa, 1 h) to 3.5 wt. % (673 K, 2.5 MPa, 10 cycles of "heating to 673 K (1 h) ⇌ cooling to 293 K (1 h)"). Apparently, the second *endo*-effect was due to the decomposition of fullerene deuteride with liberation of gaseous deuterium, which is consistent with the available published data for the decomposition of fullerene hydride.<sup>2,3</sup> The second *endo*-effect is also clearly seen in the samples of the Pd/C + Ful deuterated mixture. The small value of the first *endo*-effect (weight loss at ~385 K) for these samples is connected with the small amount of Pd in them.

There is an absorption band in the IR spectra of the deuterated samples with a maximum at 2120 cm<sup>-1</sup>,

which, according to the data of Ref. 1, is due to the stretching vibrations of the C—D bonds. This band is not observed when the sample is deuterated at room temperature\* or for the Pd/C deuterated catalyst.

It was established by chemical analysis that the deuterium content in the sample monotonically increases as the temperature, pressure, and the number of "sorption  $\rightleftharpoons$  desorption" cycles increase. The maximum content of deuterium, corresponding to the empirical formula  $C_yD_{26}$  ( $C_y$  is a molecule of fullerene  $C_{60}$  or  $C_{70}$ ), was obtained at the pressure of 2.5 MPa and by a 10-fold repetition of "heating to 673 K (1 h)  $\rightleftharpoons$  cooling to 293 K (1 h)".

This work was financially supported by the Russian Foundation for Basic Research (Project No.

96-03-33586) and the Russian Scientific Technical Program "Fullerenes and Atomic Clusters" (Project No. 96133).

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Received May 16, 1996

## A new route for decomposition of the platinum(IV) $\beta$ -ammonioethyl complex: elimination of the $\beta$ -ammonium group

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It has been established previously<sup>1</sup> that in aqueous chloride solutions the platinum  $\beta$ -ammonioethyl complex  $K[Pt(CH_2CH_2NH_3^+)Cl_5]$  (**1**) decomposes *via* two routes. In an acidic medium when the nitrogen atom of the complex is quaternized ( $pK_a \approx 8.2$ ),  $S_N2$  attack by the external nucleophile  $Y^-$  on the  $\alpha$ -C atom occurs to form the corresponding aminoethane derivative  $YCH_2CH_2NH_3^+$ . In alkaline media, aziridine is formed through intrasphere reductive elimination.

We have found that in iodide solutions ( $[NaI] = 5.0 \text{ mol L}^{-1}$ ) at 80 °C in the presence of a phosphate buffer ( $[Na_2HPO_4] = [KH_2PO_4] = 0.07 \text{ mol L}^{-1}$ ) and  $K_2PtCl_4$ , complex **1** decomposes to yield ethylene (en). Almost no ethylene forms in the absence of  $Pt^{II}$ ; the addition of  $K_2PtCl_6$  decreases considerably the rate of the accumulation of ethylene. The values of the rate constants  $k_{en}$  determined from the equation  $k_{en} = (d[en]/dt)_0/[1]_0$  from the initial rates of the formation of ethylene at the initial concentration of complex **1** of  $1 \cdot 10^{-3} \text{ mol L}^{-1}$  are the following:

Pt <sup>II</sup>	Pt <sup>IV</sup>	$k_{en} \cdot 10^6/\text{s}^{-1}$
mol L <sup>-1</sup>		
0	0	0
0.011	0	$1.20 \pm 0.04$
0.03	0	$6.4 \pm 0.4$
0.05	0	$12.9 \pm 0.3$
0.1	0	$36.8 \pm 2.3$
0.1	0.001	$3.60 \pm 0.03$
0.1	0.01	$0.40 \pm 0.02$

The results obtained agree with Scheme 1.\*

The dependence of  $k_{en}$  on  $[Pt^{II}]$  is close to quadratic, which makes it possible to assume that stages *a* and *a'* are fast. The combination of these two stages involving  $Pt^{II}$ , oxidative addition (stage *a*), and complementary reduction (stage *b*), results in the formation of the platinum(II)  $\beta$ -ammonioethyl complex. The decomposition of  $Pt^{II}CH_2CH_2NH_3^+$  by elimination of the  $\beta$ -ammo-

\* Acido ligands in Pt complexes were omitted.