The Ritter reaction in zeolite H-ZSM-5. NMR observation of the intermediate *N*-alkylnitrilium cation formed on interaction between Bu^{t}OH and MeCN

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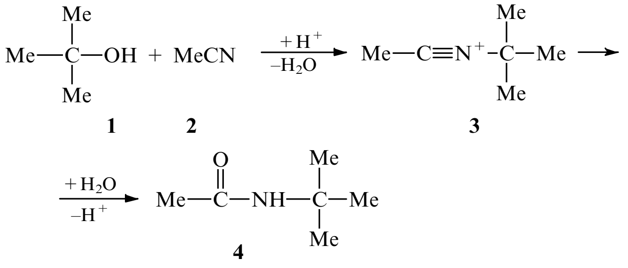
***N-tert*-Butylacetonitrilium cation as intermediate has been observed with ^{13}C CP/MAS NMR in the Ritter reaction between *tert*-butyl alcohol and acetonitrile in zeolite H-ZSM-5.**

It has been known since 1948 that the interaction of olefins (or secondary and tertiary alcohols) with alkylnitriles in acidic medium gives rise to *N*-alkylamides (the Ritter reaction).[1] It is generally accepted that the reaction proceeds *via* the formation of an intermediate *N*-alkylnitrilium cation[1] (see Scheme 1). However, so far nobody has observed the suggested intermediate cation spectroscopically in acidic solution or on an acidic solid catalyst during the reaction.



Scheme 1

In this paper we report on the identification using solid state ^{13}C NMR of the *N-tert*-butylacetonitrilium cation **3**, as the intermediate during the reaction between *tert*-butyl alcohol **1** and acetonitrile **2** to form *N-tert*-butylacetamide **4** in zeolite H-ZSM-5.[†]

Figure 1 shows CP/MAS ^{13}C NMR spectra of *tert*-butyl alcohol and acetonitrile co-adsorbed on H-ZSM-5.[‡] Comparative analysis of these spectra allow us to identify the formation of the intermediate *N-tert*-butylacetonitrilium cation **3** and the final *N-tert*-butylacetamide **4**.

If [2-^{13}C]Bu^{t}OH and unlabelled MeCN are co-adsorbed on zeolite then two intense signals from the ^{13}C-labelled carbons at 69.6 and 59.5 ppm can be identified, as well as the signal from the ^{13}C-labelled C–OH group of the unreacted alcohol at 82 ppm[3] and a weak signal from unlabelled methyl groups at 28.4 ppm from the [2-^{13}C]Bu^{t}OH and/or a reaction product (Figure 1*a*). Keeping the zeolite sample with these co-adsorbed reactants for a few days at 296 K, or heating the sample to 373 K for 30 min, results in a complete disappearance of the

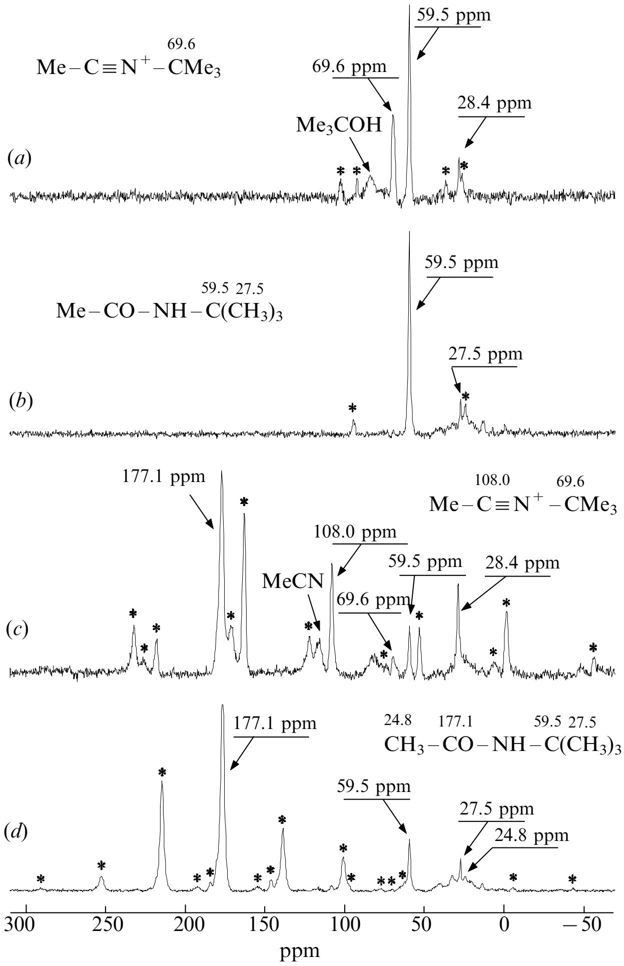


Figure 1 CP/MAS ^{13}C NMR spectra for the products formed after co-adsorption of *tert*-butyl alcohol and acetonitrile on H-ZSM-5 zeolite at 296 K: (*a*) and (*b*) show the co-adsorption of the [2-^{13}C]Bu^{t}OH (82% ^{13}C enrichment) and unlabelled MeCN. (*c*) and (*d*) show the co-adsorption of [2-^{13}C]Bu^{t}OH (10% ^{13}C enrichment) and [1-^{13}C]MeCN (80% ^{13}C enrichment). Both (*a*) and (*c*) are 4 h after co-adsorption, (*b*) and (*d*) are 4 days after co-adsorption. The spinning rate of the samples was 3.3 kHz in (*a*), 3.5 kHz in (*b*), 5.5 kHz in (*c*) and 3.8 kHz in (*d*). Asterisks (*) in the spectra denote spinning side-bands.

[†] *General experimental details.* A well-characterized H-ZSM-5 zeolite (Si:Al = 49) was activated by subsequent heating at 450 °C for 2 h in air and for 4 h under vacuum (10^{-5} torr). We then froze out equal amounts (*ca.* 300 μmol g^{-1}) of the alcohol and acetonitrile on H-ZSM-5 under vacuum at the temperature of liquid nitrogen. After sealing the glass tube with the zeolite sample from the vacuum system, the sample was slowly warmed to room temperature and kept at 296 K for a few hours before the reaction products were analysed. Analysis of the products was made directly inside the zeolite sample with CP/MAS ^{13}C NMR in a sealed glass tube inserted into an NMR zirconia rotor. ^{13}C NMR spectra with cross-polarization and magic angle spinning[2] (CP/MAS ^{13}C NMR) were acquired on a Bruker MSL-400 NMR spectrometer, operating at 100.613 MHz at 296 K. The following conditions were used for CP experiments: the proton high power decoupling field was 12 G (4.9 μs 90° ^{1}H pulse), the contact time was 3 ms under Hartmann–Hahn matching conditions (51 kHz), the delay between scans was 3 s, the number of scans ranged from 800 to 16000 and the spinning rate was 3.3–5.5 kHz. Chemical shifts were measured with respect to TMS as external reference and uncorrected for diamagnetic susceptibility. To facilitate NMR analysis and to follow selectively the transformation of each of the reactants, the alcohol, labelled with ^{13}C at the quaternary carbon atom, [2-^{13}C]Bu^{t}OH, or acetonitrile, ^{13}C-labelled at the CN group, [1-^{13}C]MeCN, were used in the NMR experiments.

[‡] Numerous spinning side-bands denoted in the spectra as asterisks (*) arise from 'slow' spinning of the sample under magic angle, not sufficient to average out large values of chemical shift anisotropy[2] $\Delta\sigma \sim$ 100–300 ppm in the C=O and CN groups of the species **2**, **3** and **4**.

signal at 69.6 ppm (Figure 1*b*); only the signal at 59.5 ppm remains in the spectrum together with a weak signal at 27.5 ppm.

In parallel, intense signals at 108.0 and 177.1 ppm from the ^{13}C-labelled carbon atoms, originating from the reacted acetonitrile, are clearly distinguished in the spectrum with co-adsorbed [1-^{13}C]MeCN (80% ^{13}C enrichment) and [2-^{13}C]Bu^{t}OH (10% ^{13}C enrichment) (Figure 1*c*). The signals at 69.6 and 59.5 ppm, which are now of essentially smaller intensity compared to the signals in Figure 1*a*, are also visible. In this spectrum the signals from both unreacted alcohol and acetonitrile are seen at 82[3] and 116[4] ppm, respectively. If the zeolite sample is left to stand for a long time with these specifically ^{13}C-labelled co-adsorbates at 296 K then the signal at 108.0 ppm disappears. Finally, only an intense signal at 177.1 ppm remains in the spectrum besides the signals of smaller intensity at 59.5 and 27.5 ppm.

Based on the analysis of the behaviour of different signals in NMR spectra with time for co-adsorbed Bu^{t}OH and MeCN we conclude that the group of signals at 27.5, 59.5 and 177.1 ppm should be assigned to the final reaction product and the signals at both 69.6 and 108.0, which disappear with time, to some intermediate in this reaction.

According to the chemical shifts the signals from the former group belong to *N-tert*-butylacetamide **4**. Indeed, the ^{13}C NMR shifts observed for **4** are in a good agreement with those reported in solutions,[§] provided that some of the carbons in the organic molecule adsorbed on acidic zeolite exhibit an additional downfield chemical shift, resulting from the interaction of these carbon atoms with Brönsted acid sites (*e.g.*, C–OH group in adsorbed Bu^{t}OH shifts additionally downfield by 13 ppm[3]).[¶]

The second group of signals disappearing with time can easily be interpreted in terms of the formation of the *N-tert*-butylacetonitrilium cation **3**. Chemical shifts for the signals disappearing with time agree well with the ^{13}C NMR characteristics for the cation **3** in solution.[††]

Thus, we were able to detect for the first time the formation of an intermediate *N*-alkylnitrilium cation in the Ritter reaction. Moreover, our experimental results clearly show that the Ritter reaction can be carried out not only in acidic solution, but also on solid acid catalyst, namely zeolite H-ZSM-5.

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[§] According to ref. 5 *N-tert*-butylacetamide **4** exhibits the following ^{13}C NMR shifts in solution: δ 23.6 (CH_3), 28.55 (CH_3, *tert*-butyl group), 49.9 (quaternary carbon), 169.0 ($C=O$).

[¶] Assignment of the ^{13}C shifts observed for the adsorbed intermediate **3** and the product **4** is given above each molecule depicted in Figure 1.

[††] We prepared the *N-tert*-butylacetonitrilium cation **3** from Bu^{t}Cl and MeCN in SbF_5/SO_2 solution.[6] It has the following ^{13}C NMR characteristics in liquid SO_2 at $-40\,^{\circ}$C. Chemical shifts: δ 3.03 (CH_3), 27.98 (CH_3, *tert*-butyl group), 65.45 (quaternary carbon), 108.20 (CN). *J*-couplings in an acetonitrile fragment of the cation (Hz): $^1J(^{13}C-^{14}N) = 40.8$, $^1J(^{13}C-^{13}C) = 60.0$, $^2J(^{13}C-^1H) = 10.6$.