Reactions of ^{12}C and ^{13}C Acetone Mixtures with a HZSM-5 Zeolite

INTRODUCTION

The reaction path of acetone conversion over solid acid catalysts has been assumed to be similar to that in homogeneous acid media; i.e., a series of aldolization and dehydration reactions occurs after protonization of the acetone molecule (1–4). Over HZSM-5 zeolites, aliphatic (especially isobutene, IB) and light aromatic compounds predominated as final products.

In the present paper, the scrambling of C atoms from the parent acetone molecules in the conversion products was studied to contribute to the knowledge of the reaction mechanism of acetone conversion over H forms of zeolites.

EXPERIMENTAL

NaZSM-5 zeolite (Si/Al = 13.5) was supplied by the Research Institute for Oil and Hydrocarbon Gases, Czechoslovakia, and transformed into the H form by acid leaching. Prior to the experiments, 0.1 g of the zeolite was dehydrated overnight in vacuum 10^{-4} Pa at 450°C. Then, 0.4–0.6 mmol g^{-1} of acetone was adsorbed at room temperature for 30 min $(^{12}CH_3)_2{}^{13}CO$ and equimolecular mixtures of $(^{12}CH_3)_2{}^{12}CO$ + $(^{12}CH_3)_2{}^{13}CO$, $(^{13}CH_3)_2{}^{13}CO$ + $(^{12}CH_3)_2{}^{12}CO$ and $(^{13}CH_3)_2{}^{13}CO$ + $(^{12}CH_3)_2{}^{13}CO$ were employed for the experiments. The ^{13}C labeled acetones were supplied by Merck, Canada, in enrichment higher than 99.4 at.%. The sample with preadsorbed acetone was heated at a linear rate (8°C min^{-1}) and the conversion products were fed directly into the vacuum system of a Finnigan 400 quadrupole mass spectrometer. Molecular ions were detected with an ionization energy of 14 eV and in some cases also of 75 eV.

RESULTS AND DISCUSSION

Characteristic TPC (temperature-programed conversion) curves recorded at low ionization energies are shown in the lower part of Fig. 1, (a) for preadsorbed nonlabeled acetone, and (b) for preadsorbed acetone labeled in the carbonyl group. In the upper part is depicted the release of CO_2 measured at 75 eV; this CO_2 contains only the carbon atom from the acetone carbonyl group (its fraction in the total amount of the products is about 10%). The molecular peaks with m/z = 56 and 57 for unlabeled and labeled parent acetone, respectively, belong to IB and exhibit two maxima. In the temperature region of the first maximum, pentenes (m/z = 70 in (a), in (b) only the most abudant peak 71 is depicted) and propylene with methylcyclohexenes (not shown in Fig. 1) are also evolved. At higher temperatures the following compounds are released: acetone (m/z = 58 for (a) and 59 for (b)) and C_{7-9} aromatics (m/z = 92, 106, and 120 for (a); for (b) only the most intensive peaks with m/z = 94, 108, and 123 are depicted).

In all cases measured, no scrambling of C atoms was found in the released acetone and, similar to those shown in Fig. 1, CO_2 always contained the C atom from the acetone carbonyl group. The isotopic composition of IB is depicted in Fig. 2 where the experimental data are compared with those calculated assuming a random distribution of ^{13}C from a complex consisting of two and/or four acetone molecules. The formation of IB over acid forms of zeolites has been
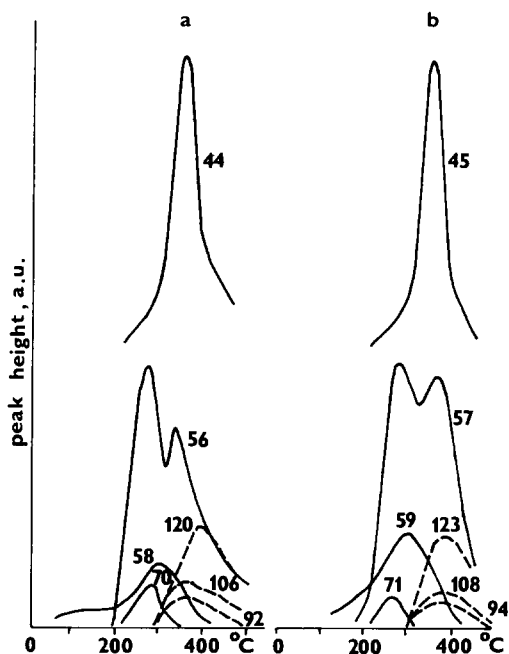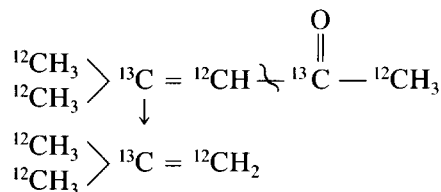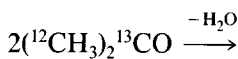
FIG. 1. MS spectra of TPC of acetone. (a) Pread-sorbed $(^{12}CH_3)_2{}^{12}CO$: (b) preadsorbed $(^{12}CH_3)_2{}^{13}CO$, up-per part—peaks of CO_2 recorded at 75 eV, $m/z = 44$ and 45 for (a) and (b), respectively. Lower part—mo-lecular peaks recorded at 14 eV: 56 (57) for IB, 58 (59) for acetone, 70 (71) for pentene, 92 (94) for toluene, 106 (108) for xylene and 120 (123) for trimethylbenzene: the m/z in brackets refer to (b), for pentenes and aromatics only the most intense peaks of isotopic molecules are given.

assumed to proceed: (i) via the decomposi-tion of diacetone alcohol, which is the pri-mary intermediate of aldol condensation (1–4), or (ii) via decomposition of its dehy-drated form, mesityloxide (3, 4), both with the aid of surface hydroxyls and simultane-ous formation of acetic acid or ketene-like intermediate, and/or (iii) via the cracking of a higher condensate, which yields, in addi-tion to IB, an oxygen-containing surface in-termediate firmly bonded to the zeolite (3, 5). The experiments with ^{13}C labeling (Fig. 2) support the assumptions that IB is formed via the decomposition of a surface conden-sate in which no scrambling of C atoms oc-curs. Thus, e.g., IB formed from $(^{12}CH_3)_2{}^{13}CO$ (Fig. 2b) contains only one ^{13}C

atom which corresponds to the following reaction:

$$2(^{12}CH_3)_2{}^{13}CO \xrightarrow{-H_2O}$$

$$\begin{matrix} ^{12}CH_3 \\ ^{12}CH_3 \end{matrix} \Big\rangle\, ^{13}C = {}^{12}CH \searrow {}^{13}C - {}^{12}CH_3$$
$$\big\downarrow \qquad\qquad \overset{\|}{\underset{}{O}}$$

$$\begin{matrix} ^{12}CH_3 \\ ^{12}CH_3 \end{matrix} \Big\rangle\, ^{13}C = {}^{12}CH_2$$

All the experimental data shown in Figs. 2a–2d confirm that IB consists of C atoms of one acetone molecule and one methyl group of another acetone molecule. Con-trary to IB, the isotopic composition of pro-pylene and pentene, which in Fig. 3 repre-sent the other aliphatic products of acetone conversion, exhibits a significant scram-bling of ^{13}C atoms of parent acetone mole-cules. This supports the assumption (1, 3) that these compounds are formed via sec-ondary reactions of IB. However, due to a relatively low amount of these products and decreased sensitivity of the mass spectrom-eter when measuring molecular peaks at 14 eV, the experimentally found isotopic com-position is not precise enough to decide whether the best fit is obtained with the cal-culated random distribution of labeled C from IB (of experimentally found isotopic composition) or from parent acetone mole-cules.

The same limitation holds for the determi-nation of the molecular peaks of the aro-matic compounds. In Fig. 4, the experi-mental values for toluene, xylenes, and trimethylbenzenes from the parent $(^{12}CH_3)_2{}^{13}CO$ are compared with those cal-culated assuming a condensation reaction of one propylene and one IB molecules to toluene (both of experimental isotopic com-position; see Figs. 2 and 3, respectively), two IB molecules (of experimental isotopic composition, Fig. 2) to xylenes, and three parent acetone molecules to trimethylben-zenes. It follows that under our experimen-tal conditions these reactions do not occur.
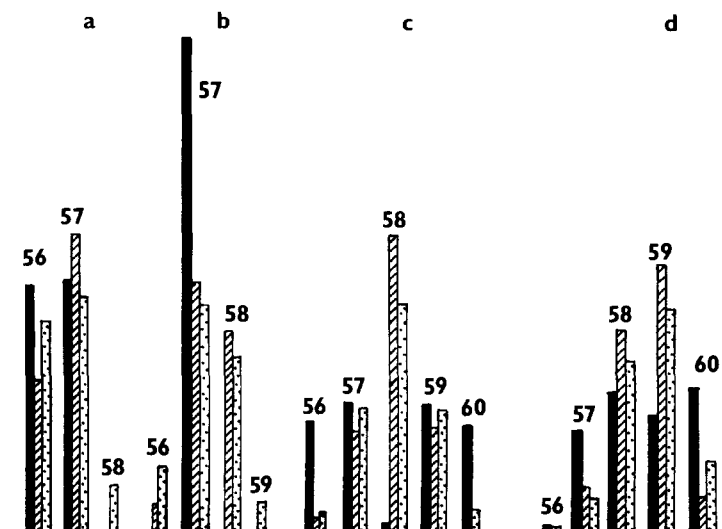
FIG. 2. Isotopic composition of isobutene. Molecular peaks: (a) 1 : 1 mixture of $(^{12}CH_3)_2^{12}CO$ and $(^{12}CH_3)_2^{13}CO$: (b) only $(^{12}CH_3)_2^{13}CO$: (c) 1 : 1 mixture of $(^{12}CH_3)_2^{12}CO$ and $(^{13}CH_3)_2^{13}CO$: (d) 1 : 1 mixture of $(^{12}CH_3)_2^{13}CO$ and $(^{13}CH_3)_2^{13}CO$. (■) experimental data: (▨) data calculated assuming a random distribution of ^{13}C from two acetone molecules; and (░) from four acetone molecules.
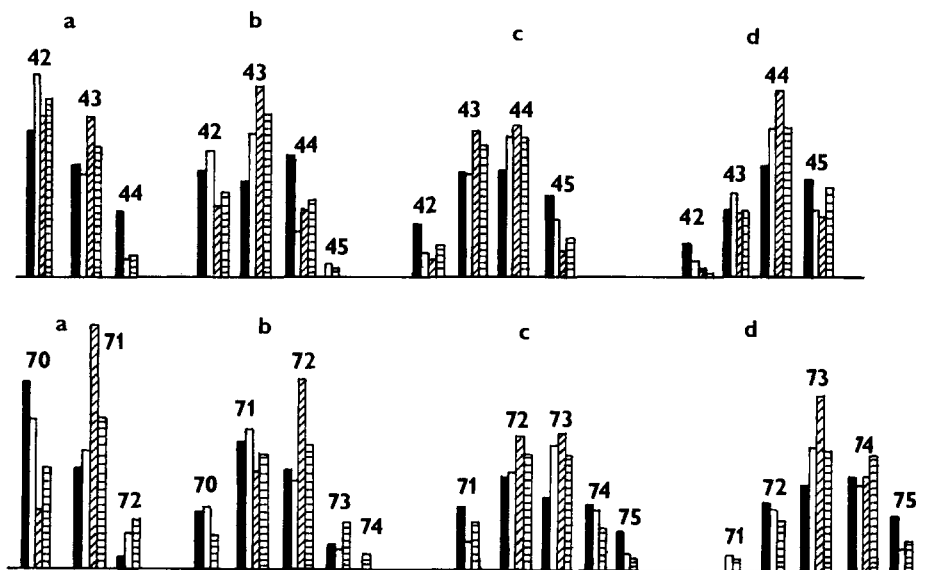

FIG. 3. Isotopic composition of propylene and pentenes. Molecular peaks, (a), (b), (c), and (d) as in Fig. 2. (■) experimental data; data calculated assuming a random distribution of ^{13}C from: (▯) two IB molecules of experimental isotopic composition, (▨) from two parent acetone molecules, and (▤) from six parent acetone molecules.
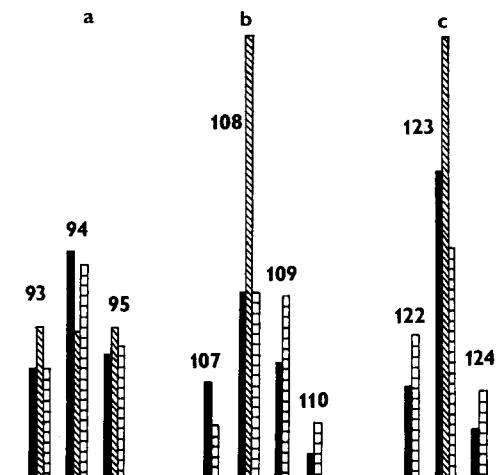
FIG. 4. Isotopic composition of toluene (a), xylene (b), and trimethylbenzene (d) formed in the conversion of $(^{12}CH_3)_2$ ^{13}CO. Molecular peaks, (■) experimental data, (▨) data calculated assuming a condensation reaction of IB and propylene (both experimental isotopic composition) to toluene, two IB (experimental isotopic composition) to xylene, and three parent acetones to trimethylbenzene, (▤) assuming a random distribution of ^{13}C from six parent acetone molecules.

If they proceed, then, e.g., trimethylbenzenes should have only three ^{13}C atoms that were not observed. Better agreement is obtained with a random distribution of labeled C atoms from at least six parent acetone molecules (this was confirmed with all acetone mixtures, not shown in Fig. 4). Therefore, a series of secondary reactions of various C fragments is most probably operating in the formation of these aromatics.

CONCLUSIONS

Using mixtures of variously labeled ^{13}C acetones it was found that:

(i) Isobutene is composed of three atoms from one parent acetone molecule and one C atom from the methyl group of another acetone molecule. The reaction most probably occurs via the decomposition of diacetone alcohol or mesityloxide-like intermediates in which no scrambling of C atoms takes place.

(ii) The isotopic composition of the other aliphatic compounds can be satisfactorily described assuming secondary reactions of isobutenes, or fragments of acetone molecules, as shown for propylene and pentenes.

(iii) Aromatic compounds formed have an isotopic composition corresponding to a random distribution of ^{13}C atoms from at least six parent acetone molecules which agrees with the assumption of a series of parallel and consecutive reactions leading to the creation of these compounds.

(iv) Small amounts of CO_2 released during TPC contain only the C atoms from the parent acetone carbonyl group; this probably originates from the decomposition of an acetate-like species.

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