Collision-Activated Dissociation Spectra for the Characterization of the Diels-Alder Adducts between C_<60> and Troponoids

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Collision-Activated Dissociation Spectra for the Characterization of the Diels-Alder Adducts between C_{60} and Troponoids

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Diels-Alder adducts of C_{60} easily cycloreverted to the starting materials by heating. This property makes it difficult to determine the molecular weight of adducts by means of mass spectrometry. We employed collision-activated dissociation spectra to characterize the Diels-Alder adducts of C_{60} with troponoids, cycloheptatriene, and 2-cycloalkenones and their acetals since the molecular peak of C_{60} as well as peaks derived from C_{60} were intense. This technique is useful for the determination of the molecular weight of thermally labile compounds.

Introduction

Recently, a number of works on the thermal reactions of buckminsterfullerene (C_{60}) with dienes such as anthracene,[1] cyclopentadiene,[2] isobenzofurans,[3] tropones,[4] and indene,[5] were intensively investigated to obtain Diels-Alder adducts for functionalization of C_{60}. These adducts, however, easily cycloreverted to the starting materials by heating. In order to elucidate the structure, mass spectrometry was sometimes used for assessment of elemental analysis because of a small quantity of the adducts or some difficulties of purification of the adducts.
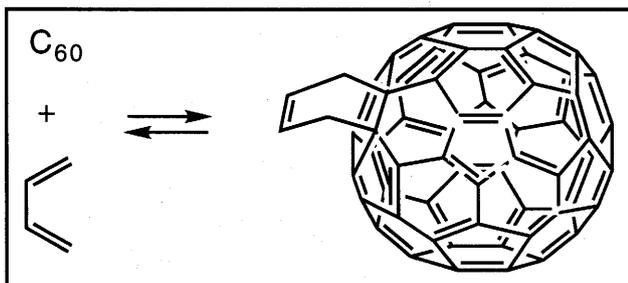
In the most cases, mass spectroscopic techniques for C_{60} adducts, however, were not always satisfactory. The only observable peaks were those of C_{60} because of facile cycloreversion of adducts. We applied here the collision-activated dissociation (CAD) experiments to the Diels-Alder adducts of C_{60} and troponoids, cycloheptatriene, and 2-cycloalkenones and their acetals to determine the structures.

Results and Discussion

All mass spectra were acquired with a JEOL SX/SX102A tandem mass spectrometer of BEBE geometry, which was controlled by a JEOL DA-7000 data system (Tokyo, Japan). Positive- and negative-ion fast atom bombardment (FAB) mass spectra were obtained by using the former spectrometer. Ions were produced by bombardment with a neutral xenon atom at 5 kV. The mass range (m/z 1-1000) was scanned at 5 s under an ion source accelerating potential of 10 kV, and averaged intensities in decade scans were recorded. The pseudo molecular ions generated by FAB MS were selected as precursor ions, and collided with argon molecules in the third field-free region. The argon pressure was sufficient to attenuate the primary ion beam by 50%. The fragment ions were dispersed by the second spectrometer and the spectra were recorded as the FAB MS/MS spectra.

Figure 1 shows the positive-ion FAB mass spectrum for the Diels-Alder adduct (**1a**) between C_{60} and tropone (**2**) with m-nitrobenzyl alcohol matrix, in which an ion peak at m/z 720 due to C_{60} was observed with strong intensity, whereas the molecular peak $[M+H]^{+}$ at m/z 827 was quite weak. From these results, it would be difficult to conclude whether the ion peak at m/z 720 is a fragment peak from the adduct or not.

Figure 2 shows the positive-ion FAB MS/MS spectrum of **1a**, in which the $[M+H]^{+}$ ion at m/z 827 was observed as a base peak together with the $[M+H-C_7H_6O]^{+}$ peak at m/z 721 with strong intensity. These results imply that the peak at m/z 721, assignable to C_{60}, was the fragment peak of the base peak at m/z 827. Therefore, it was concluded that **1a** is a 1:1-adduct between C_{60} and **2**. Similarly, the adducts between C_{60} and other troponoids showed the intense molecular ion peak in the FAB MS/MS spectra. Typical fragment peaks of **1** as well as those of the adducts (**3**, **4**) between C_{60} and cycloheptatriene are summarized in Table 1. In positive-ion FAB MS, intensity of the molecular ion was weak, whereas that in FAB MS/MS spectra was strong. Thus, the positive ion
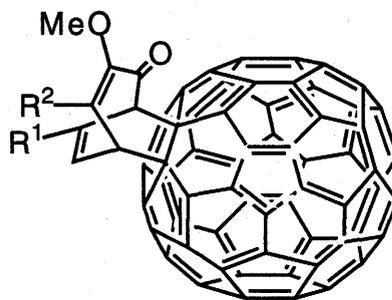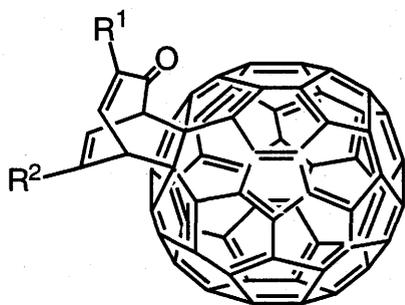
1a $R^1=R^2=H$
1b $R^1=OMe, R^2=H$
1c $R^1=Br, R^2=H$
1d $R^1=H, R^2=OAc$
1e $R^1=H, R^2=OMe$

1f $R^1=R^2=OMe$
1g $R^1=OMe, R^2=Br$
1h $R^1=OMe, R^2=Cl$
1j $R^1=OMe, R^2=i\text{-}Pr$
1k $R^1=OMe, R^2=CO_2Bu\text{-}n$
1m $R^1=R^2=Cl$

1n $R^1=i\text{-}Pr, R^2=H$
1p $R^1=H, R^2=i\text{-}Pr$

2

5 n = 1
7 n = 2

6 n = 1
8 n = 2

3

4

9

10

11 R = O
13 R $<^H_{OH}$

12
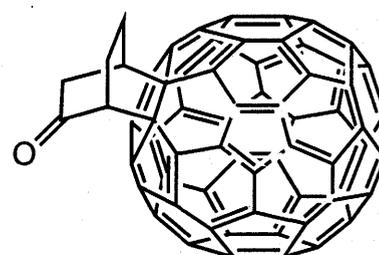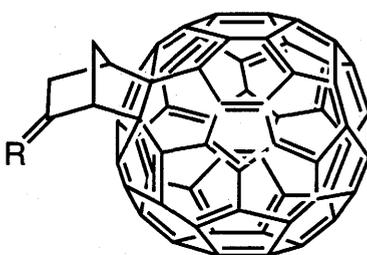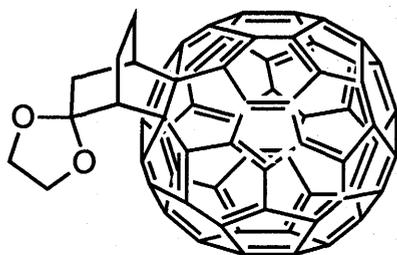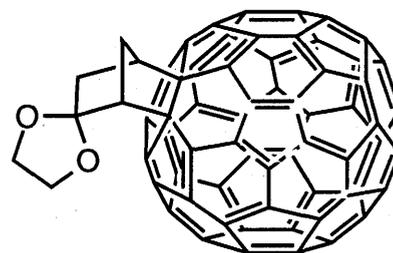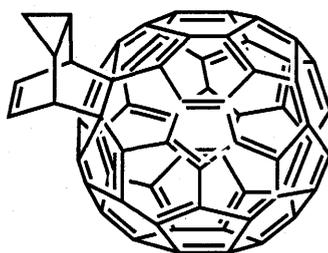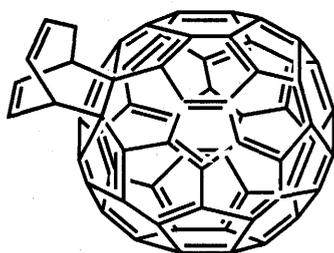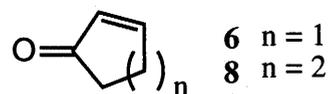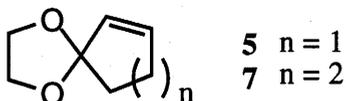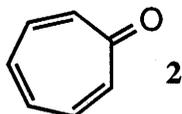
Figure 1. Positive-ion FAB MS Spectrum of **1a**.

Figure 2. Positive-ion FAB MS/MS Spectrum of **1a**.

Table 1. Typical Fragment Peaks (m/z, relative intensity) of **1**, **3**, and **4** Measured by Positive FAB MS and FAB MS/MS

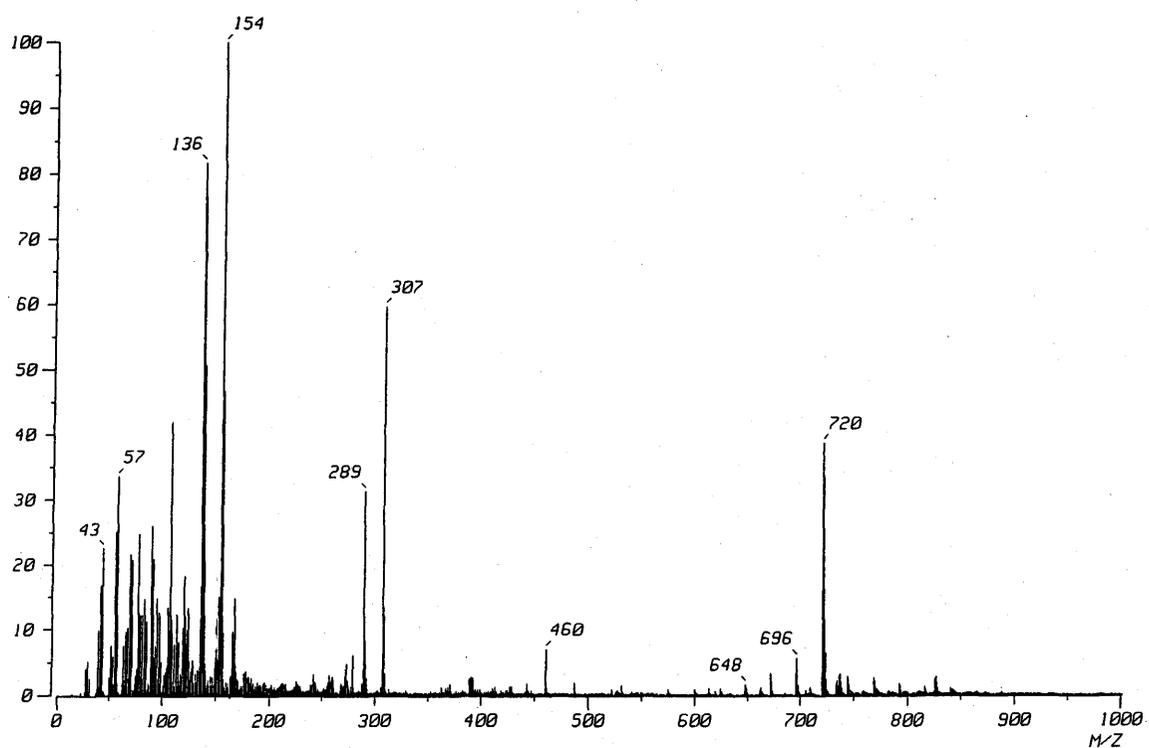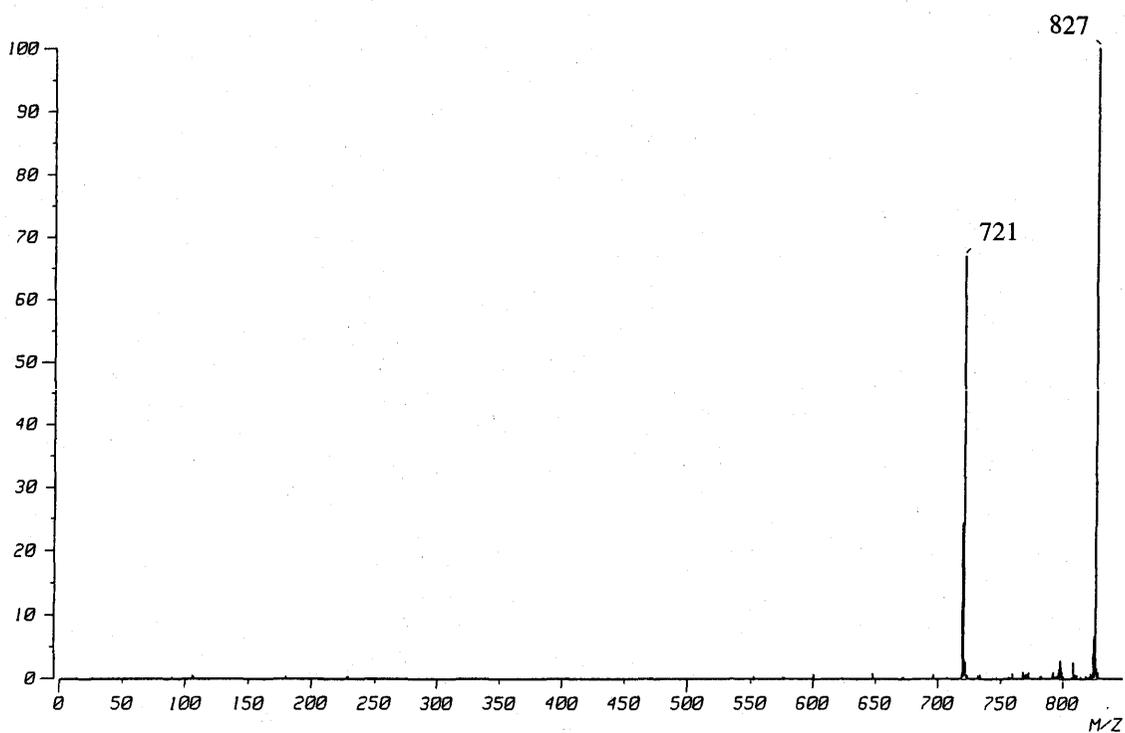| Compound	Positive FABMS[a]	FAB MS/MS
1a ($C_{67}H_6O$, 826)	827 (3), 826 (3), 721 (34), 720 (39), 392 (13), 391 (47)	827 (100), 721 (67)
1b ($C_{68}H_8O_2$, 856)	857 (1), 856 (1), 721 (29), 720 (35)	857 (100), 721 (62), 720 (16)
1c ($C_{67}H_5OBr$, 904, 906)	907 (0.5), 906 (0.6), 905 (0.5), 904 (0.4), 721 (13), 720 (15)	907 (100), 721 (60), 720 (12)
1d ($C_{69}H_8O_3$, 884)	885 (3), 884 (3), 723 (11), 722 (27), 721 (55), 720 (63)	885 (100), 721 (84), 720 (27)
1e ($C_{69}H_8O_2$, 856)	857 (1), 856 (1), 721 (12), 720 (14)	857 (100), 721 (67), 720 (32)
1f ($C_{69}H_{10}O_3$, 886)	887 (2), 886 (1), 722 (14), 721 (32), 720 (36)	887 (100), 721 (72)
1g ($C_{68}H_7O_2Br$, 934, 936)	937 (1), 936 (1), 935 (1), 722 (14), 721 (32), 720 (39)	937 (100), 936 (2), 721 (64)
1h ($C_{68}H_7O_2Cl$, 890, 892)	892 (0.6), 891 (0.8), 890 (0.7), 721 (16), 720 (19)	891 (100), 721 (51)
1j ($C_{71}H_{14}O_2$, 898)	899 (1), 721 (12), 720 (14)	899 (100), 721 (46), 720 (11)
1k ($C_{73}H_{16}O_4$, 956)	957 (1), 956 (1), 722 (13), 721 (26), 720 (32)	957 (100), 721 (86), 720 (20)
1m ($C_{67}H_4OCl_2$, 894, 896, 898)	899 (0.4), 897 (1), 895 (1), 721 (15), 720 (18)	898 (5), 896 (100), 895 (5), 722 (12), 720 (11)
1n ($C_{71}H_{14}O_2$, 898)	899 (2), 722 (21), 721 (46), 720 (53)	899 (100), 721 (57)
1p ($C_{71}H_{14}O_2$, 898)	899 (2), 898 (2), 722 (20), 721 (43), 720 (50)	899 (100), 721 (73), 720 (19)
3 ($C_{67}H_8$, 812)	813 (4), 812 (3), 723 (14), 722 (26), 721 (45), 720 (49), 663 (19), 662 (12), 674 (12), 429, 391, 281, 221	813 (100), 812 (37), 811 (34), 721 (87)
4 ($C_{67}H_8$, 812)	813.0 (1), 721 (13), 720 (15)	813 (100), 721 (70)

[a] The base peak was observed at m/z 307 or 154, which are due to m-nitrobenzyl alcohol used for matrix.

Table 2. Typical Fragment Peaks (*m/z*, relative intensity) of **9-13** Measured by Positive FAB MS and FAB MS/MS

Compound	Positive FABMS[a]	FAB MS/MS
9 ($C_{67}H_{10}O_2$, 846)	848 (0.1), 847 (0.2), 846 (0.2), 721 (0.7), 720 (0.8)	847 (100), 721 (15)
10 ($C_{68}H_{12}O_2$, 860)	863 (0.2), 862 (0.3), 861 (0.5), 720 (1)	861 (100), 721 (24)
11 ($C_{65}H_6O$, 802)	804 (6), 803 (11), 802 (9), 721 (29), 720 (35)	803 (100), 721 (79)
12 ($C_{66}H_8O$, 816)	818 (4), 817 (8), 816 (6), 721 (13), 720 (16)	817 (100), 721 (77), 720 (34)
13 ($C_{65}H_8O$, 804)	805 (10), 804 (19), 721 (20), 720 (23)	805 (100), 721 (81)

[a] The base peak was observed at *m/z* 307 or 154, which are due to *m*-nitrobenzyl alcohol used for matrix.

Table 3. Thermal Stability of the Adducts of C_{60} and 2-Cycloalkenones and their Acetals

|	145 °C	150 °C	160 °C	165 °C	170 °C
9	-	15 h, no CR[a]	8 h, < 5% decomp	-	-
10	5 h, no CR	-	-	15 h, no CR	-
11	-	4 h, no CR	15 h, no CR	15 h, < 2% decomp	-
12	-	4 h, no CR	10 h, no CR	-	15 h, ~1% decomp

a: no CR means no cycloreversion.

FAB MS/MS spectrum gave an important information about the structure of the cycloadducts.

Table 2 summarizes mass spectral data of the adducts (**9-12**) of C_{60} and 2-cycloalkenones (**5, 7**) and their acetals (**6, 8**).[6] The molecular peaks as well as the peak due to $[C_{60}+H]^+$ at *m/z* 721 were quite weak in the FAB MS, while the molecular peaks observed in FAB MS/MS were so strong that the adducts (**9-12**) were 1:1-adducts between C_{60} and **5-8**. Interestingly, the peak intensity of C_{60} was lower in **9** and **10** than the adducts of troponoids and C_{60}.

Furthermore, compounds **11** and **12** showed an intense peak of C_{60} in FAB MS/MS spectra. This means that the cycloreversions of **9** and **10** were more efficiently hindered than those of **11** and **12**. This observation is consistent to the carbonyl group of **11** and **12** more easily isomerizing to an enol form than the corresponding acetal group, from which cycloreversions would occur.

These stabilities in mass spectra were parallel to the results of the thermal reactions of the adducts of C_{60} as shown in Table 3.[6] Adduct **11** was stable on heating at 160 °C for 15 h. Heating **9** at 160 °C for 8 h, 5% of C_{60} were detected by HPLC, whereas the adducts (**1a-1c**) of troponoids and C_{60} cycloreverted to C_{60} and tropones by heating in *o*-dicholorobenzene at 160 °C for 30 min.
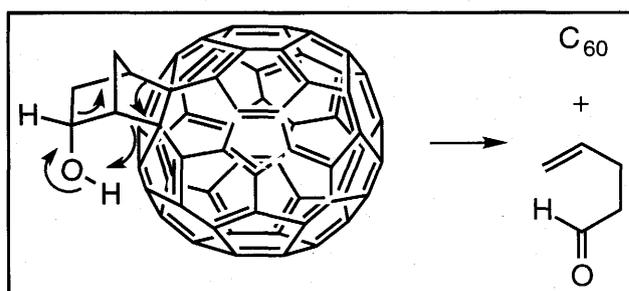
As shown in Table 3, the thermal stability of adducts is also sensitive to the ring system; bicyclo[2.2.1]heptane systems are less stable than bicyclo[2.2.2]octane systems. This would be arisen from ring strain.

Thermal stability of **1 3** in MS spectrometry was closer to that of ketone **11** than acetal **9**. This must be accounted for assistance of the hydroxyl group to reproduce C_{60} and C_5H_8O as shown above.

In summary, FAB MS/MS measurement is exceedingly useful technique to observe the molecular ion peak of thermally labile compounds.

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