Muon Spin Rotation of Carbonyl Compounds, an Exploration of the Mechanism of Hyperfine Interaction

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The relationship between the muon electron hyperfine coupling constant and the C═O bond stretching frequency of a series of organic carbonyl compounds at 300K has been investigated. A linear relationship is shown to exist between these two properties, but for the aromatic carbonyl compounds only. This observation is shown to be in agreement with the presently accepted hyperconjugative mechanism of the hyperfine interaction in these systems. Muonium addition to the ring systems of these compounds was also observed and the hyperfine frequencies assigned and discussed.

Introduction

Detection and characterization of radical species with exceptional sensitivity is now possible using spin-polarized muons and single-particle counting techniques.[1] The acronym μSR stands for muon spin rotation, relaxation, and resonance, covering the various ways in which the evolution of the muon polarization is studied. Similar to conventional magnetic resonance, characteristic frequencies provide measurements of internal magnetic or hyperfine parameters; relaxation functions give information on their fluctuation due to intra- and intermolecular motion. The muon spin plays the role of a nuclear spin, but the spectroscopy proves to be equally sensitive both to muons in electronically diamagnetic environments and to those which experiences a hyperfine coupling with paramagnetic electrons, the latter being of importance to the strategies involving organic radicals. The chemical reactions of muonium, mimicking those of atomic hydrogen, form the basis of muonium chemistry. Particularly important in this context has been the study of muonium-substituted organic radicals, formed by muonium addition to double or triple bonds. Several publications describing the μSR techniques are available in the literature, including a couple of journal special issues.[2−6]

There are a number of studies reporting muonium adducts with carbonyl groups.[7−21] Addition to −C═O groups contrast with the adducts formed with C═C groups due mainly to the presence of lone pairs of electrons on the oxygen atom. Muonium addition to C═C results in the complete opening of the double bond, with the unpaired electron residing mainly in a carbon $2p_z$ orbital β to the muon site. Theoretical studies for example predict an energy barrier to rotation of ca. 3 kJ mol^{-1} for the muonated ethene radical,[22] with the energy minimum corresponding to C−Mu eclipsing the p_z orbital containing the unpaired electron.

Muonium addition to a C═O bond appears different.[23,1] The muon attaches to a lone pair of electrons on the oxygen atom as would a proton and will be a position in the nodal plane of the C═O π-bond, the unpaired electron occupying the LUMO, the π* orbital of the C═O bond, of the parent molecule. Such a mechanism of addition, made possible by the presence of lone pairs of electrons on the oxygen, results in only a partial breaking of the C to O π bond. This results in a lower-energy configuration when compared with a mechanism of addition similar to that in the case of C═C where the radical formation results in the full opening of the double bond. A further consequence of the above mechanism of addition to C═O is a very small hyperfine coupling constant due to the muon occupying a position close to the nodal plane of the π* orbital containing the unpaired electron. Any libration of the O−Mu bond out of this plane thus results in an increase in the hfc due to finite overlap between this bond and the π* orbital.

Following Heller and McConnell,[24] this effect has been expressed by the following equation for the isotropic coupling constant:[15,20]

$$\langle A'_{\mu}(\gamma)\rangle_j = A + B\langle \cos^2 \gamma\rangle_j \qquad \text{with } j = 1, ..., 2n + 1 \qquad (1)$$

where j corresponds to the torsional eigenfunctions and the phenomenological coefficients A and B are said to correspond to transmission of spin density through-bond ("spin polarization") and through-space ("hyperconjugation") processes, respectively. Macrae et al.[20] have used the above equation to explain the temperature dependence of the hyperfine interaction of the C═O adducts and have identified the first example of a negative muon coupling constant[21] by invoking competition between the effects of spin polarization and hyperconjugation.

A closer look at these coupling effects in the case of C═O adducts shows that the spin polarization will be mainly confined to a σ-bonding pathway and the hyperconjugation to the π-bonding pathway. Furthermore, the maximisation of the hyperconjugation by a libration of the muon out of the nodal plane is resisted in this case by the presence of a partial π bond between C and O in the radical. Therefore a systematic way of preferentially perturbing the C═O π bonding should provide a method of investigating the hyperconjugative mechanism of hyperfine coupling in C═O adducts. Here we report such an investigation which uses vibrational spectroscopy to estimate the variation in C═O π bond strengths.

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We exclude from the present study any consideration of the MuCO radical,[25,26] which has the muon connected to the carbon atom and shows a very large hyperfine interaction, very different in character from the rest of the carbonyl adducts.

Experimental Section

All samples were obtained from the Aldrich or Avocado chemical companies and were used without further purification. Most samples were liquid at ambient temperatures and were run at $T = 300$ K, the rapid tumbling of the molecules automatically giving a spherical average over any anisotropy in hyperfine parameters, i.e., yielding the isotropic contact term directly, as usual. The liquids were deoxygenated by several freeze−pump−thaw cycles before being sealed under vacuum into spherical thin-walled glass bulbs of varying sizes, dependent upon sample size, but typically ca. 10 mL in volume. Only benzophenone was run as a solid and has been the subject of a more detailed study.[19] For the present purposes, the isotropic hyperfine constant for benzophenone was taken to be the appropriate average value from the single crystal study.[19]

The μSR spectra were recorded in the GPD instrument on the μE4 decay muon beamline at PSI, Switzerland, and the emitted positrons detected using scintillator counters. To correlate a positron decay with a muon incident on the sample, the experiment was run in time differential mode, in which the incoming muon starts a clock at $t = 0$ and, in so doing, triggers a gate signal of 10 μs length (a few muon lifetimes) during which no further muons can be counted. When the decay positron of the muon is measured at time $t = t$, a count at time t is added to the histogram for the given detector in which the positron was detected. While limiting the count rate of events to ca. 5×10^4 muons per second, this technique provides the necessary time resolution to measure relatively high muon spin rotation frequencies of radicals (up to ca. 500 MHz). However, the fixed time resolution available results in some loss of amplitude toward the higher frequencies[3]. Therefore, the observed radical yields were corrected using the expression given by Roduner et al [27] for the given time resolution of 1.5 ns.

The vibrational spectra of these compounds were most conveniently obtained using the Raman spectroscopic technique. Raman spectra at a resolution of 2 cm^{-1} were measured in order to determine the ν_{CO} of the closed-shell molecular species. The reported C═O stretching frequencies were determined from the maxima of the measured peaks, from a Bruker Raman FTS-66 spectrophotometer, with a laser excitation wavelength of 1064 nm. Typical Raman spectra of carbonyl compounds are to found in the literature.[28]

Results and Discussion

It was planned to preferentially perturb the strength of either the π or σ bond by a suitable choice of compound in order to test the hyperconjugative mechanism of hyperfine interaction in muonium adducts of compounds containing C═O groups. The magnitude of the muon electron hyperfine coupling was measured using muon spin rotation experiments of the neat liquid samples. The strength of the C═O bond of the parent compound was measured using FT-Raman spectroscopy (Table 1), where ν(C═O) is a good group frequency[28] with the normal mode confined mainly to the C═O bond. There are no methods available at present to measure the frequency of this bond in the open shell compound. However, if one assumes the fraction of the double bonding strength lost by an addition of an electron to the antibonding π* orbital of these carbonyl compounds to be the same, the measurable C═O stretching frequency of the parent compound may be considered as a measure of the remaining double bond character.

TABLE 1: Comparison of A_μ after Mu Addition with ν_{CO} of Closed-Shell Parent

sample	A_μ CO addition/MHz	ν_{CO}/cm^{-1}
3-bromobenzaldehyde	10.17(7)	1699
benzaldehyde	12.68(2)	1701
benzoyl cyanide	17.47(3)	1683
4-chloroacetophenone	17.92(3)	1688
2-fluoroacetophenone	18.04(3)	1689
3-fluoroacetophenone	18.30(116)	1691
4-chromanone	18.47(41)	1691
acetophenone	20.54(18)	1685
2-methylacetophenone	21.19(34)	1686
4-fluoroacetophenone	21.35(1)	1686
4-methylacetophenone	21.78(3)	1682
benzophenone	42(1)	1661
	31.8(1)[a]	1652[a]
dibenzosuberone	50.66(91)	1646

[a] Numerically averaged value of hfc obtained from the anisotropic values measured in the single crystal μSR study of benzophenone[19] Both the hfc and ν_{CO} were found to be sensitive to the molecular environment.

The vibrational stretching frequency of the C═O bond is, to a good first approximation, an estimate of the combined strength of the σ and π bonds. However, the magnitude of the hyperfine coupling constant of the muon adduct via a hyperconjugative mechanism should be determined by the strength of the π bond, since the σ-bond provides free rotation about itself.

Muon spin rotation studies of a series of carbonyl compounds with only aliphatic groups attached to the C═O group have been reported in the literature,[7−9,11] Therefore only the vibrational spectra of these materials were needed for this investigation. The electronic effects of the aliphatic groups attached to a C═O group will have to be conveyed via the σ-bonds and therefore to a good first approximation it will affect only the σ-bond strength of the C═O group. The σ bond being cylindrically symmetrical should allow free rotation about the bond axis. A change of its bond strength is thus not expected to have an effect on the torsional motion about CO bond, which is responsible for the out-of-nodal-plane motion of the muon. Therefore, one would not expect a systematic correlation between the strength of the C═O bond and the muon hyperfine coupling constants for these aliphatic carbonyl molecules. This is as observed experimentally (Figure 1).

A different scenario is to be expected for the case of the aromatic carbonyl compounds. In total, 17 samples were studied, spanning a range of related aromatic carbonyl compounds in which the C═O bond strengths varied significantly, from the observation of the differences in the vibrational spectra (a range of ca. 60 cm^{-1} in ν_{CO}; i.e., ca. 7% change in bond strength). Many of these systems displayed muonium addition to both the aromatic ring and the carbonyl site, thus showing some degree of selectivity which was also found to vary between samples. Indeed, some samples displayed complete selectivity for either the carbonyl or the ring groupings. The experimental data are given in Tables 2 and 3, and some representative spectra are shown in Figures 2−4. The vertical scales in all of the reported spectra are given in arbitrary units of polarization in Fourier power spectra and are used only as references for peaks within a sample; no normalizations were performed by using an internal standard for example, and so, no comparison is made of absolute intensities between samples. The nature of the power spectrum exaggerates differences in peak intensities, including the effects of the instrumental band-pass, as mentioned above.

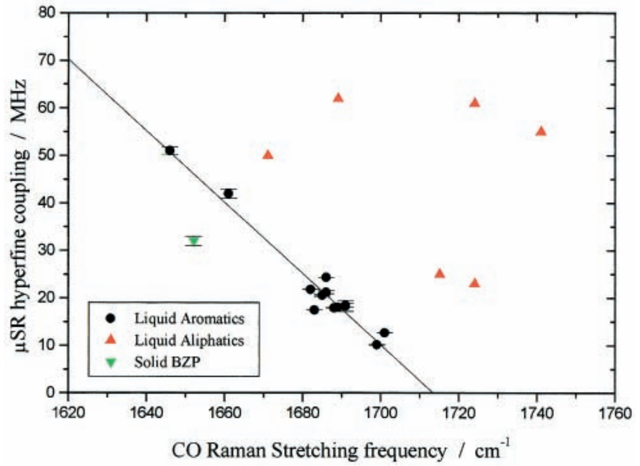


Figure 1. Correlation of closed-shell ν_{CO} with open-shell A_μ for various carbonyl species. Data of aliphatic species from ref 11. (Acetaldehyde: 23 MHz, 1724 cm^{-1}; acetone: 25 MHz, 1715 cm^{-1}; formamide: 50 MHz, 1671 cm^{-1}; ethyl acetate: 55 MHz, 1741 cm^{-1}; methylformate: 61 MHz, 1724 cm^{-1}; ditertiarybutyl ketone: 62 MHz, 1688 cm^{-1}.)

TABLE 2: Selectivity of Mu Addition to CO with Respect to a Nonweighted Selectivity Based on the Number of Addition Sites

sample	observed addition to C═O (% of total radical yield)	nonweighted probability of addition to C═O (%)
3-bromobenzaldehyde	100	20
benzoyl cyanide	100	13
dibenzosuberone	100	11
4-chloroacetophenone	52	20
benzaldehyde	50	17
4-chromanone	49	20
4-fluoroacetophenone	48	20
4-methylacetophenone	48	20
acetophenone	41	17
2-fluoroacetophenone	27	20
2-methylacetophenone	18	20

TABLE 3: Assignments of Ring-Adducts of Mu Addition to Aromatic Carbonyls[a]

	A_μ (MHz)		
sample	ortho	meta	para
acetophenone	446.92(1)	507(1)	476.36(1)
benzaldehyde	438.79(26)	492(1)	460.74(40)
4-methylacetophenone	476.55(6)	487.55(6)	Ø
4-fluoroacetophenone	485.50(12)	489.44(28)	Ø
4-chloroacetophenone	481.02(11)	481.02(11)	Ø
2-fluoroacetophenone	460.79(8)	477.67(50) 484(1)	469(1)
2-methylacetophenone	457.10(15)	486.40(66) 493.86(24)	474(1)
benzoyl Isocyanate	449.02(2)	–	473(1)
2-benzoyl-5-norbornene	446.75(100)	479.26(100)	474.5(100)
benzoyl chloride	450.76(11) 469.92(6)	511.16(45)	487.56(43)
benzyl acetone	492.57(6)	511.35(1)	500.71(9)
4-chromanone	417(1)	417(1) 446.63(91)	446.63(91)

[a] Ø indicates the site of existing substituents. No addition was observed to occur at such ipso sites in this study, but this has previously been shown to produce radical yields of <3× that of C−H sites[11].

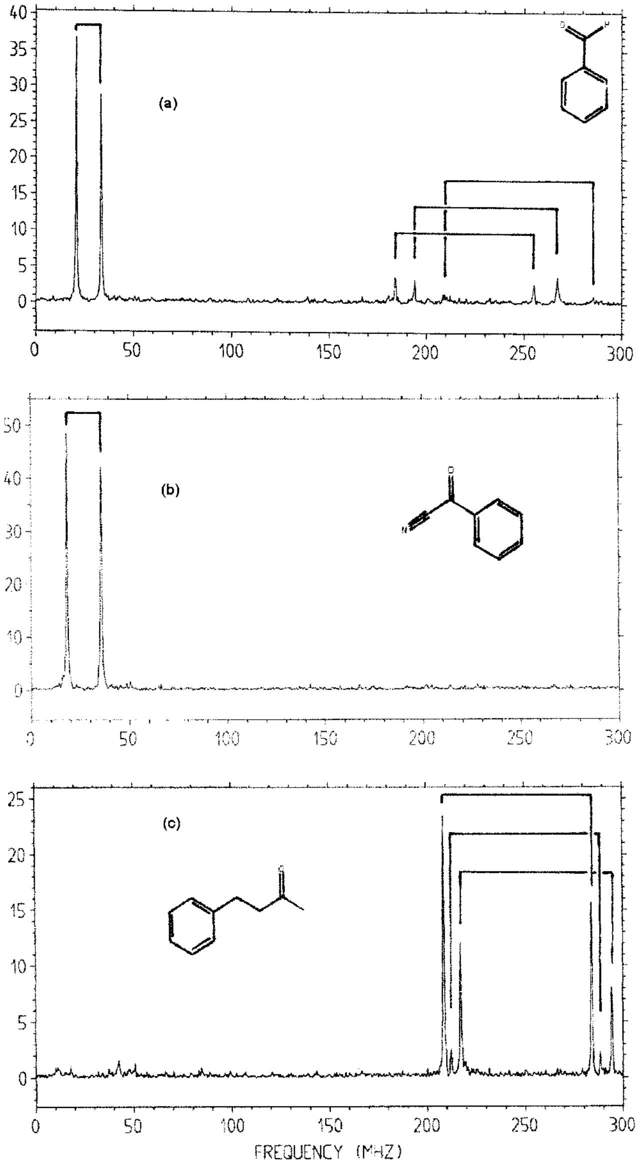


Figure 2. Representative TF−MuSR spectra of aromatic carbonyls under an applied field of 2 kG. (a). Benzaldehyde: Four radical species were observed with peaks at 20.67, 30.35, 183.91, 193.79, 210, 254.86, 266.97, and 285 MHz, relating to A_μ's of 12.68(2), 438.79(26), 460.74(40), and 492(1) MHz, indicating addition to both the CO group and the three ring positions. (b) Benzylcyanide*:* Only one radical species was observed, that of addition to the CO group, with peaks at 18.28 and 35.75 MHz, relating to A_μ = 17.47(3) MHz. (c) Benzylacetone: Only radical species due to ring addition were observed, with peaks at 208.51, 212.23, 217.05, 284.05, 288.47, and 294.30 MHz, relating to A_μ = 492.57(6), 500.71(9), and 511.35(1) MHz.

Literature data[15,20,21] on the variation of hfc with temperature relates to the perturbation of the $\langle\cos^2\gamma\rangle_j$ term of eq 1 by changing the population distribution of the energy level manifold of the C−OMu torsional vibration. The present study uses a series of samples kept at the same temperature, thus keeping the population distributions almost constant. (A better approximation to this will be hfc extrapolated to zero temperature.) However, the amplitude of the torsional motion is varied by changing the strength of the C═O π-bond, as measured using vibrational spectroscopy. A measure of the electron density at the C═O bond is reflected in its strength.

Muonium addition to the carbonyl group of the aromatic compounds was found to result in a difference in the hfc of ca. 40 MHz across the range of ν_{CO} and displayed a linear correlation with a negative gradient as shown in Figure 1. It is interesting to note that this is the type of variation that would be expected if $\langle A'_\mu(\gamma)\rangle_j$ is plotted against $\langle\cos^2\gamma\rangle_j$ according to eq 1. Note that the dihedral angle γ is defined such that at γ = 0 the O−Mu bond eclipses the symmetry axis of the carbon

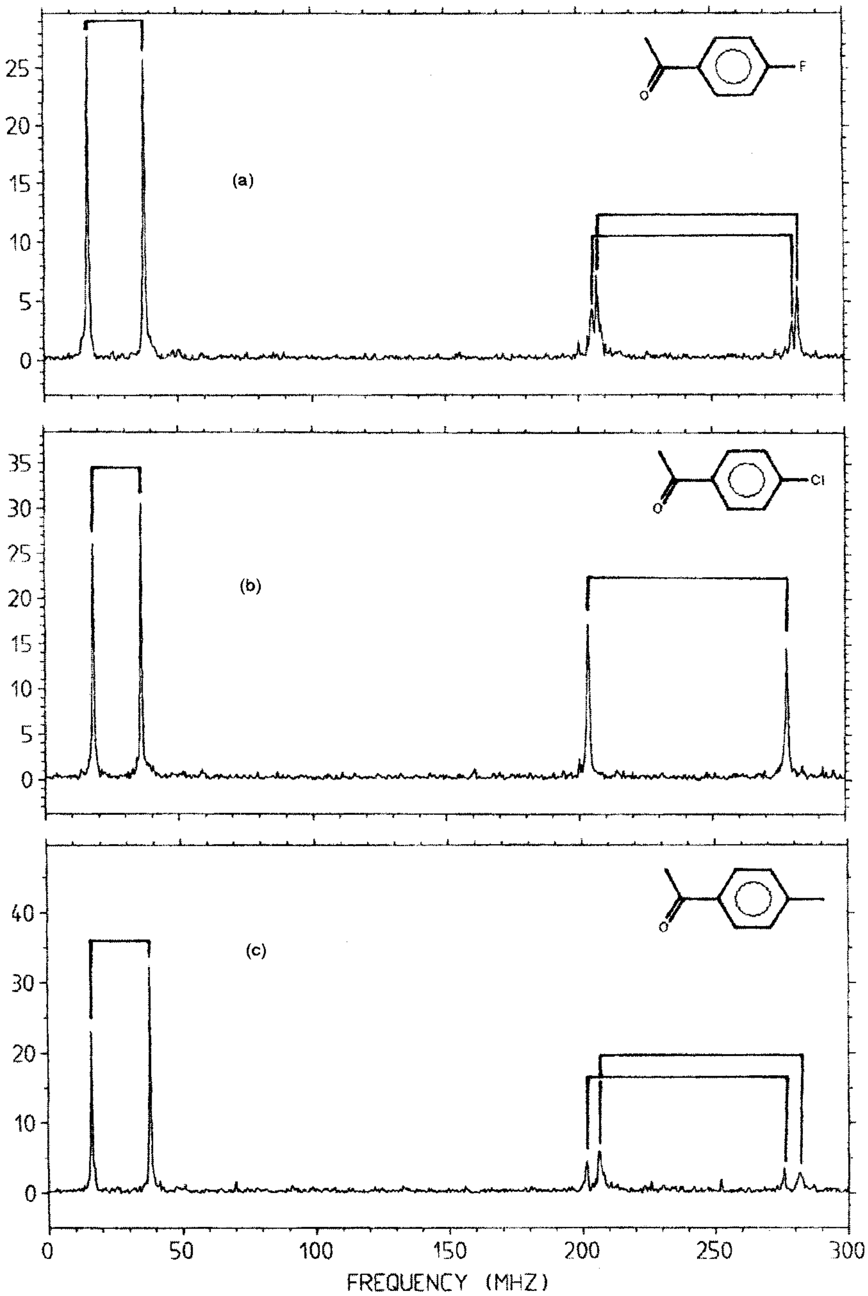


Figure 3. TF−MuSR spectra of various monosubstituted *p*-acetophenone−Mu species. All spectra were recorded at 2 kG. (a) 4-Fluoroacetophenone: Three radical species were observed with peaks at 16.35, 37.70, 205.22, 207.15, 280.28, and 282.27 MHz, relating to A_μ's of 21.35(1), 485.50(12), and 489.44(28) MHz. (b) 4-Chloroacetophenone: Two radical species were observed with peaks at 18.05, 35.97, 203.25, and 277.76 MHz, relating to A_μ's of 17.92(3) and 481.02(11) MHz. (c) 4-Methylacetophenone: Three radical species were observed with peaks at 16.13, 37.91, 201.36, 206.18, 275.52, and 281.37 MHz, relating to A_μ's of 21.78(3), 476.55(6), and 487.55(6) MHz.

p_z orbital in which, in the simplest schematic representation of the radical's electronic structure, the unpaired electron notionally resides.[24] More theoretical work is needed before drawing any more conclusions from this correlation because the linearity of the plot may be a consequence of the small ranges of bond strengths and hyperfine interactions explored in this investigation.

Benzophenone presents an interesting case in which muonium addition to the carbonyl group leads to a greater isotropic hfc in a diethyl ether solution than in the numerically averaged values found in the solid (Figure 1). The values corresponding to the solid benzophenone shows the largest deviation from the correlation presented in Figure 1. This indicates the limitations of the validity of this correlation to the liquid or solution states, where the molecules are relatively free. The observed hfc of C−O−Mu in the solid state in this case is significantly smaller than that anticipated from the measured value of the CO stretching frequency. This deviation is therefore likely to be due to solid-state intermolecular interactions that provides an additional restriction mechanism to the librational motion of the carbonyl−muonium adduct, an effect which is absent in the free molecule in the liquid or solution state.[19]

The Mu addition to these compounds also displayed a range of site selectivities, with some species displaying exclusive carbonyl or alternatively, ring addition. The selectivity toward carbonyl addition is reported in Table 2 and was found to vary considerably as a function of ring substituent. Clearly, competing reactions between the implanted Mu atoms and the closed-shell system exist for different addition sites within the molecules.

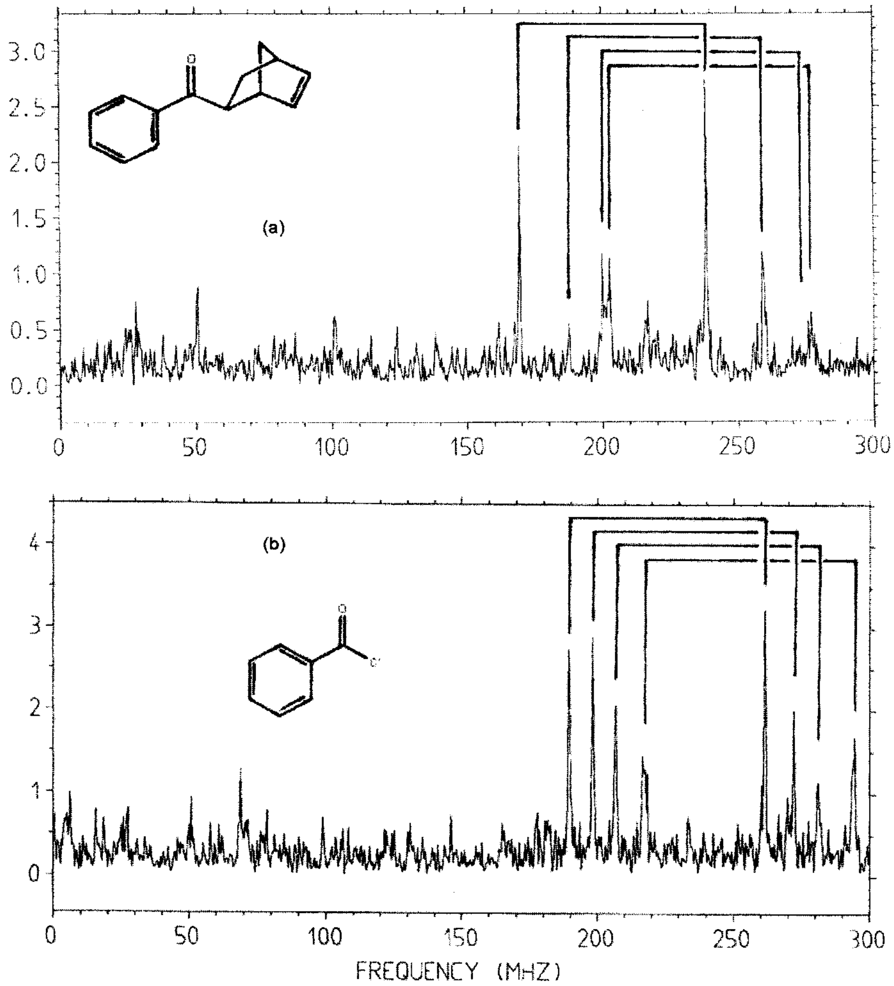


Figure 4. Further examples of muonium addition to aromatic carbonyls. Again, both spectra were recorded under a field of 2 kG. (a). 2-Benzoyl-5-norbornene: Four radical species were observed with peaks at 169.44, 186.5, 200, 202.54, 238.27, 259.55, 274, and 278 MHz, relating to A_μ's of 407.71(4), 446.75(100), 474.5(10), and 479.26(100) MHz, indicating addition to both the three aromatic ring positions and the C═C double bond of the unsaturated ring. (b) Benzoyl Chloride*:* Four radical species were observed with peaks at 189.37, 198.15, 206.34, 217.10, 261.38, 271.76, 281.19, and 294.03 MHz, relating to A_μ's of 450.76(11), 469.92(6), 487.56(43), and 511.16(45) MHz. The degeneracy of the two ortho sites adjacent to the carbonyl grouping is lifted by the presence of the chloride.

Mu addition to the aromatic rings in these compounds also showed distinct differences from sample to sample. An assignment is given here for the observed adduct hfc frequencies, following earlier work[29] reviewed by Rhodes,[5] and listed in Table 3. Simple ideas of inductive and mesomeric effects provide the assignment of, for example, the three observed frequencies of 447, 476, and 507 MHz for the acetophenone molecule to the ortho, para, and meta adducts, respectively. These assignments may be compared with the hyperfine frequency of 514.4 MHz, observed for muonium addition to pure liquid benzene.[29,31,32] The apparent anomaly of the presence of only one frequency for the adducts to 4-chloroacetophenone (Figure 3) finds an explanation when this spectrum is compared with those of 4-fluoro and 4-methyl substituted compounds, when it is clear that what is observed is an unresolved pair of very similar frequencies for the two sites.

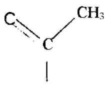
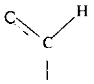
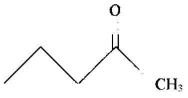
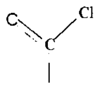
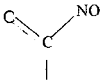
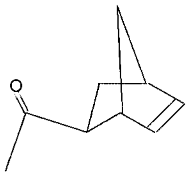
General conclusions that can be drawn from Table 3 are that the highest frequency resonance can in most cases be assigned to the adducts to the meta position with respect to the carbonyl grouping, where the least perturbation of the electron density due to the carbonyl group is expected. The lowest frequency being that due to the adduct to the ortho position, where the largest withdrawal of electron density is to be expected. The para position falls approximately midway between these two extremes.

An additional resonance is observed in 2-benzoyl-5-norbornene (Figure 4a), which consists of two ring systems, one of which is aromatic (see Table 3) with the other having only a single, isolated C═C double bond. The hfc for radicals at the nonaromatic double bond site was found to be 407.71(4) MHz—approximately 100 MHz lower than that for the aromatic sites. Benzoyl chloride (Figure 4b) is also an interesting case in that four nonequivalent ring sites were resolved, where, on the grounds of symmetry, only three may be expected. The assignment accounts for a lifting of degeneracy of the two ortho sites of ca. 19 MHz, possibly due to a considerable π character of the carbonyl-to-ring bond or to through-space effects of the neighboring group. The meta sites are then degenerate within the experimental resolution and are assigned to the coupling of ca. 511 MHz.

Roduner[29] has devised a qualitative method of accounting for the observed hyperfine frequencies for muonium adducts to monosubstituted phenyl rings. This expresses the difference between the value for pure benzene and the monosubstituted phenol using the following equation, where A_μ^0 = 514.4 MHz and is the measured hfc for Mu addition to benzene and Δ_X is the relevant perturbation term:

$$A_\mu = A_\mu^0 \prod_9 (1 - \Delta_X) \qquad (2)$$

TABLE 4: Effects of Substituents upon the Hyperfine Coupling Constants of Mu Ring Adducts[a]

Substituent	$100\Delta_X$		
	ortho-	*meta-*	*para-*
	13.15	1.48	7.43
	14.73	4.39	10.47
	4.17	0.52	2.59
	12.30 8.58	0.55	5.14
	12.74	-	8.08
	13.18	6.87	7.79

[a] Values listed in terms of Δ_X, eq 1; see text for detials

The carbonyl species examined in this study provides an extension to the functionalities listed by Roduner[29] for monosubstituted ring systems (Table 4). This concept has been extended by Rhodes and Roduner[33] to polysubstituted radicals. The combined stability of a radical due to the presence of more than one substituent is found to be unequal to the sum of the stabilizations due to individual substituents. This effect was named "captodative" stabilization. Therefore, in the case of polysubstitution, allowance has to be made for interactions between the ring substituents by the use of a modified equation where Δ_{XY} is the intergroup coupling (Table 5):

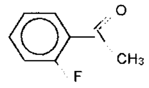
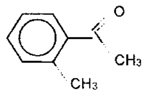
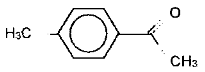
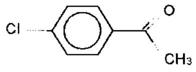
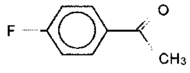
$$A_\mu = A^0_\mu \prod_X (1 - \Delta_X) \prod_{XY} (1 - \Delta_{XY}) \qquad (3)$$

The review of the literature by Rhodes[5] concludes that the captodative proposal is borne out, by citing the cases where there is the possibility of direct conjugation between the two substituents and the radical center. None of the examples studied in the present investigation satisfies this criterion, and therefore, none is expected to provide evidence for the captodative effect. Indeed, the observed variation in sign of Δ_{XY} is complicated, as expected for the complexity of the effects of substituents on spin delocalization.

Conclusion

Selective perturbation of the π and σ bonds of the C=O group by the choice of suitable compounds has made it possible to obtain a linear correlation between the bond strength, as measured by vibrational spectroscopy, and the muon hfc constant for systems with conjugated C=O bonds. This linear correlation resembles the expression for the isotropic coupling constant proposed by Heller and McConnell[24] and thus may be considered as confirmation of the accepted theory of hyperfine coupling for these systems. A study involving detailed temperature variations of the hyperfine coupling parameters of all these carbonyls may be useful for further exploration of these mechanisms.

TABLE 5: Substituent-Coupling Effetcs upon Mu Addition[a]

Substituent	$100\Delta_{XY}$		
	ortho-	*meta-*	*para-*
	-3.66	0.19 (3) 4.02 (5)	-0.79
	3.34	-0.84 (3) -0.97 (5)	4.47
	-7.74	-1.08	-
	-8.73	-0.19	-
	-9.20	-2.27	-

[a] Values tabulated in terms of Δ_{XY}, eq 2. Bracketed terms in the meta column refer to the ring site number.

The muonium addition to the aromatic ring often results in a full complement of adducts from possible ring sites, with the magnitudes of the hfc being in the order meta > para > ortho with respect to the position of the carbonyl group.

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