7096 *J. Phys. Chem. A* **2001,** *105,* 7096–7105

Addition vs Abstraction Reactions of the Methyl Radical with Nitrones, Alkenes, Aldehydes, and Imines

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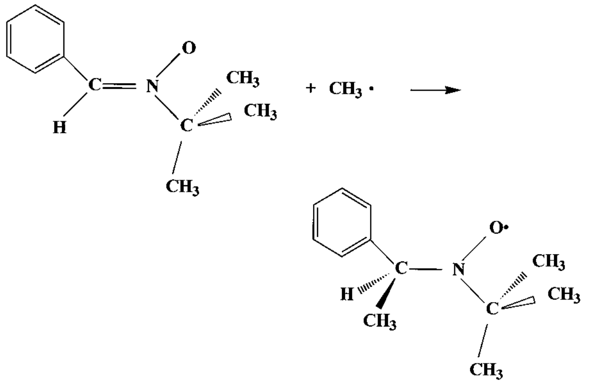
Received: March 1, 2001; In Final Form: May 7, 2001

In continuation of our theoretical study of spin trapping, we have compared the abilities of nitrones, imines, aldehydes, and alkenes to add the methyl radical vs their tendency to have protons abstracted by this radical. This study confirms that for nitrones, whereas abstraction of the iminyl H is exothermic with a low activation energy, addition is even more favored, both thermodynamically and kinetically, with the addition occurring at the unsaturated carbon. For alkenes, the preferred process is also addition, but the reactions are considerably less exothermic and have higher activation energy barriers than those for nitrones. Aldehydes favor abstraction; the bulkier the group on the carbonyl carbon, the more the abstraction is preferred over addition. Imines are intermediate between alkenes and aldehydes in their tendency toward addition and abstraction. As a result, they can undergo either process, and the favored route entirely depends on the substituents present; moreover, addition can occur to either the carbon or the nitrogen with appropriate substituents.

Introduction

Spin traps are compounds which “capture” reactive radicals to form more stable radical products. Among commonly used spin traps are the class of compounds known as nitrones, which readily add radicals at the unsaturated carbon.[1] For example, one of the most traditionally used nitrones is PBN (C-phenyl-N−*tert*-butylnitrone), which reacts as shown in Scheme 1.

SCHEME 1



On the other hand, imines do not serve as spin traps. Thus, radicals such as the *tert*-butoxyl radical do not add to the iminyl double bond in aldimines; instead, they abstract the iminyl hydrogen, −CH=N−.[2] Why is there no similar hydrogen atom abstraction from nitrones? This is the question that prompted the present study.[3] To attempt to answer it, we have examined the relative enthalpies of addition vs abstraction in simple nitrones and imines. For comparison, aldehydes and alkenes were included in the study: in aldehydes, there is no evidence for addition, only fast hydrogen abstraction,[4] whereas in alkenes, only radical addition, no abstraction, is known to occur.[5] Thus, in the series below, experimental data suggest the following relative reactivities: nitrone > alkene > imine > aldehyde for radical addition and nitrone < alkene < imine < aldehyde for hydrogen abstraction. Specifically,[2] styrene, $C_6H_5{-}CH{=}CH_2$, and C-phenyl-N−*tert*-butylnitrone, $C_6H_5{-}CH{=}N(O){-}C_4H_9$, experience radical addition only but benzaldehyde, $C_6H_5{-}CH{=}O$, and benzylidine imines, $C_6H_5{-}CH{=}N{-}R$, experience hydrogen abstraction only.

Is it purely reaction enthalpies that dictate these relative reactivities? Or do activation-energy barriers play the more significant role? To answer these questions, we have also considered enthalpies of activation for each of the reaction types. Therefore our approach has been to compare the reactions as shown in Scheme 2.

The reacting radical ($R^{\bullet}$) which was chosen for this investigation is the methyl radical, $CH_3^{\bullet}$. The model radical traps (for the addition reactions) and model hydrogen radical donors (for the abstraction reactions) comprised the simplest compounds containing the relevant functional groups, i.e., nitrone, $CH_2{=}N(O)H$, methyl imine, $CH_2{=}NH$, methanal $CH_2{=}O$, and ethene, $CH_2{=}CH_2$. (The term “nitrone” is old nomenclature for “methylidenamine oxide”. We use the old term herein for simplicity. Also, it should be noted that the structure, $CH_2{=}N(O)H$, is a minor tautomer of an oxime. Although it is a legitimate structure, it has not been experimentally observed; it was used in this study as a device to explore the chemistry while controlling the computational cost.) As well, substituted compounds (substituents included various aliphatic groups and the phenyl group) were used in order to observe the effect of substituents on the enthalpies of reaction and activation associated with the addition and abstraction reactions. Furthermore, because it is known experimentally that H abstraction also occurs from the N-alkyl group in imines,[2] the ΔH_{rxn} and, in some cases, the $\Delta H^{\ddagger}$ were determined for the formation of radical products of these N-substituted compounds.

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10.1021/jp0108115 CCC: $20.00

SCHEME 2

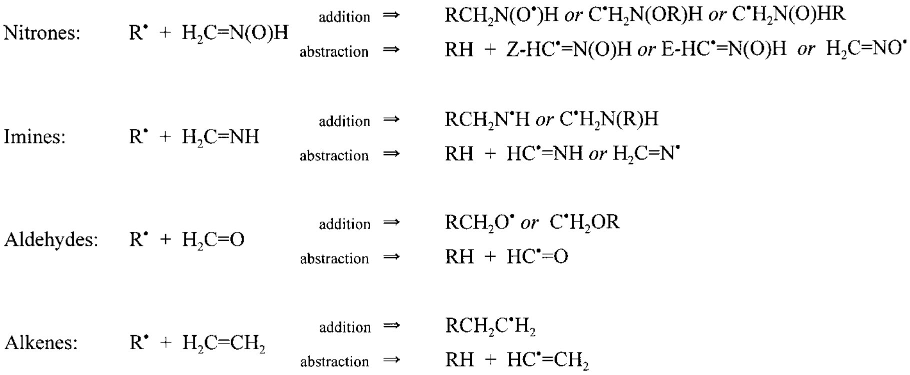


TABLE 1: Addition of $CH_3^•$ to Imine: Reaction and Activation Enthalpies (kJ/mol) at Various Levels

			A addition at C $CH_3^• + H_2C{=}NH \rightarrow CH_3CH_2N^•H$		B addition at N $CH_3^• + H_2C{=}NH \rightarrow H_2C^•{=}NHCH_3$	
energy	geometry optimization	frequency analysis	$\Delta H^‡$	ΔH_{rxn}	$\Delta H^‡$	ΔH_{rxn}
HF/6-31G(d)	HF/6−31G(d)	HF/6−31G(d)	39	−93	73	−56
HF/6-31+G(d,p)	HF/6-31+G(d,p)	HF/6-31+G(d,p)	46	−82	78	−51
MP2(full)/6-31G(d)	MP2(full)/6-31G(d)	HF/6-31G(d)	68	−82	92	−76
MP2/6-31+G(d,p)	MP2/6-31+G(d,p)	HF/6-31+G(d,p)	70	−73	91	−77
B3LYP/6-31G(d)	B3LYP/6-31G(d)	B3LYP/6-31G(d)	20	−95	32	−88
B3LYP/6-31+G(d,p)	B3LYP/6-31+G(d,p)	B3LYP/6-31+G(d,p)	25	−82	37	−83
B3LYP/6-311G(d,p)	B3LYP/6-31G(d)	B3LYP/6-31G(d)	24	−81	34	−82
B3LYP/6-311+G(2df,p)	B3LYP/6-31G(d)	B3LYP/6-31G(d)	27	−76	40	−79
B3LYP/6-311+G(3df,2p)	B3LYP/6-31G(d)	B3LYP/6-31G(d)	27	−75	40	−78
CBS−RAD(B3LYP/6-31G(d))	B3LYP/6-31G(d)	B3LYP/6-31G(d)	23	−81	42	−82
G2	MP2(full)/6-31G(d)	HF/6-31G(d)	32	−78	50	−78

TABLE 2: Abstraction of $H^•$ by $CH_3^•$ from Imine: Reaction and Activation Enthalpies (kJ/mol) at Various Levels

			C abstraction of E−H $CH_3^• + H_2C{=}NH \rightarrow CH_4 + HC^•{=}NH$ (*Z*)		D abstraction of Z−H $CH_3^• + H_2C{=}NH \rightarrow CH_4 + HC^•{=}NH$ (*E*)		E abstraction of N−H $CH_3^• + H_2C{=}NH \rightarrow CH_4 + H_2C{=}N^•$	
energy	geometry optimization	frequency analysis	$\Delta H^‡$	ΔH_{rxn}	$\Delta H^‡$	ΔH_{rxn}	$\Delta H^‡$	ΔH_{rxn}
HF/6-31G(d)	HF/6−31G(d)	HF/6−31G(d)	111	−2	105	−15	77	−106
HF/6-31+G(d,p)	HF/6-31+G(d,p)	HF/6-31+G(d,p)	113	3	107	−12	81	−92
MP2(full)/6-31G(d)	MP2(full)/6-31G(d)	HF/6-31G(d)	91	0	81	−23	62	−52
MP2/6-31+G(d,p)	MP2/6-31+G(d,p)	HF/6-31+G(d,p)	88	5	79	−21	61	−37
B3LYP/6-31G(d)	B3LYP/6-31G(d)	B3LYP/6-31G(d)	37	−25	27	−44	5	−92
B3LYP/6-31+G(d,p)	B3LYP/6-31+G(d,p)	B3LYP/6-31+G(d,p)	41	−21	28	−41	12	−79
B3LYP/6-311G(d,p)	B3LYP/6-31G(d)	B3LYP/6-31G(d)	39	−27	29	−45	8	−81
B3LYP/6-311+G(2df,p)	B3LYP/6-31G(d)	B3LYP/6-31G(d)	43	−24	34	−41	16	−75
B3LYP/6-311+G(3df,2p)	B3LYP/6-31G(d)	B3LYP/6-31G(d)	44	−25	34	−41	16	−74
CBS−RAD(B3LYP/6-31G(d))	B3LYP/6-31G(d)	B3LYP/6-31G(d)	52	−20	43	−38	22	−73
G2	MP2(full)/6-31G(d)	HF/6-31G(d)	61	−15	51	−34	31	−69

Computational Method

A detailed study of the imine systems (addition of the methyl radical to methyl imine and abstraction of $H^•$ from methyl imine by the methyl radical) with various theoretical procedures and basis sets was done to ascertain the appropriate theoretical level to be used in other systems (Tables 1 and 2). For small species, all energies and geometries were determined at the G2 level of theory,[6,7] a method known to provide reliable bond dissociation energies. However, some of the systems studied were not amenable to the computationally demanding G2 calculations on our computers. Therefore, on the basis of the results reported in Tables 1 and 2 which will be discussed below, the complete set of data was obtained from B3LYP/6-311+G(2df,p) single points at the B3LYP/6-31G(d) geometries and frequencies. The Gaussian 98[8] program was used throughout.

Zero-point energies (ZPE) were scaled by 0.9806[9] for the B3LYP/6-31G(d) frequencies and by 0.8929[10] within the G2 series of calculations to correct for overestimation of vibrational frequencies. Enthalpies were calculated as described previously,[11] with no correction for low-frequency torsional modes.

Results and Discussion

Choice of the Method. Enthalpies of reaction and activation determined at various levels of theory for the addition of the methyl radical to methyl imine, $H_2C{=}NH$, are presented in Table 1. Note that $CH_3^•$ can in principle add to either the carbon or the nitrogen of methyl imine (reactions A and B, respectively). Enthalpies of reaction and activation for the abstraction of $H^•$ from methyl imine by $CH_3^•$ are given in Table 2. For the latter, three different H atoms can theoretically be abstracted, the trans (*E*) hydrogen on the carbon, the cis (*Z*) hydrogen on the carbon, and the H on the nitrogen; these are presented as reactions C, D, and E, respectively. For each system, the starting materials, the transition-state structures, and the products were

TABLE 3: Spin-Squared Expectation Values, ⟨S^2⟩, UHF/6-31G(d), for Reactions in Tables 1 and 2

reaction	$CH_3^\bullet$ radical	TS	product
A: addition: $CH_3^\bullet + H_2C=NH \rightarrow CH_3CH_2N^\bullet H$	0.761	1.01	0.76
B: addition: $CH_3^\bullet + H_2C=NH \rightarrow H_2C^\bullet=NHCH_3$		1.01	0.76
C: abstraction: $CH_3^\bullet + H_2C=NH \rightarrow CH_4 + HC^\bullet=NH$ (*Z*)		0.93	0.88
D: abstraction: $CH_3^\bullet + H_2C=NH \rightarrow CH_4 + HC^\bullet=NH$ (*E*)		0.91	0.85
E: abstraction: $CH_3^\bullet + H_2C=NH \rightarrow CH_4 + H_2C=N^\bullet$		0.96	0.99

optimized at the theoretical level indicated in column 2, with frequency analyses at the level shown in column 3 and energies at the level presented in column 1. Table 3 presents the spin-squared expectation values at the HF/6-31G(d) level for the reactants, transition states, and products of the reactions A−E in Tables 1 and 2.

The G2 results are used as the benchmark. As is well-known,[12] the Hartree−Fock results are not reliable for enthalpy changes; they are, however, included for comparison. The MP2 calculations greatly overestimate the activation enthalpies. When spin contamination is low (as for the starting materials and the addition products, Table 3), the ΔH_{rxn}'s from the MP2 calculations agree reasonably well with the G2 results; however, when spin contamination is high (⟨S^2⟩ > 0.8 at the HF level, as for the abstraction products, Table 3) the MP2 data for ΔH_{rxn} are considerably less exothermic than those of G2. In general B3LYP/6-31G(d)//B3LYP/6-31G(d) gives lower activation enthalpies, and more exothermic reaction enthalpies, than those of G2. The B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) results are slightly better. However, the single-point B3LYP/6-311+G(2df,p) energy calculations at the B3LYP/6−31G(d) geometries have $\Delta H^\ddagger$ and ΔH_{rxn} which approach the G2 results and are computationally efficient. Little improvement is gained by using single-point B3LYP/6-311+G(3df,2p). The CBS−RAD[13] results are probably the most accurate in the series (more so even than G2), because the CBS−RAD method considers spin contamination in the radicals. Indeed, when spin contamination is low, as for the enthalpies of reaction for the addition of methyl to methyl imine, the ΔH_{rxn}'s from either the CBS−RAD or G2 methods are very close; on the other hand, when there is significant spin contamination (⟨S^2⟩ > 0.8), as in the transition state structures for both addition and abstraction and for the reaction enthalpies for the abstractions, there is considerable difference between the CBS−RAD and G2 results, with the CBS−RAD having generally lower activation barriers and more exothermic reaction enthalpies.

On the basis of this study, all enthalpies were determined at the computationally efficient B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d) level. This yields reaction enthalpies which are close to the results obtained with the CBS−RAD method (3−5 kJ/mol less exothermic when ⟨S^2⟩ < 0.8 and 2−4 kJ/mol more exothermic when ⟨S^2⟩ > 0.8); the results are a little further on average from those found by the G2 method (differing from 2 to −1 kJ/mol when ⟨S^2⟩ < 0.8, and from −6 to −9 kJ/mol when ⟨S^2⟩ > 0.8). Activation enthalpies obtained with B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d) are less endothermic than the CBS−RAD enthalpies (by 2−9 kJ/mol), with one exception, and are always less endothermic than the G2 activation enthalpies (by 5−18 kJ/mol). That is, the heights of the reaction barriers calculated by B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d) are underestimated relative to those calculated at both CBS−RAD and G2 levels. However, the B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d) results are closer to the CBS−RAD results in general than are the G2 results.

It is worth noting that, although the numerical values for the enthalpies differ among the various theoretical levels presented in Tables 1 and 2, all levels above Hartree−Fock predict the same addition or abstraction to be favored. For example, irrespective of the level considered, the data in Table 1 suggest that addition of the methyl radical to methyl imine could occur at either the C or N position with essentially equal enthalpies of reaction, but addition at the N position would have a higher reaction barrier; therefore, addition would preferentially occur at the C position. The data in Table 2 suggest that abstraction of the H bonded to the nitrogen is favored at all levels over abstraction of either the cis or trans H bonded to carbon, that the reaction barrier is lowest, and the reaction is the most exothermic, for abstraction of the nitrogen H, that the cis-H abstraction has an intermediate barrier and exothermicity, and that the trans-H abstraction has the highest barrier and is least exothermic.

Abstractions of H Atoms from within the Functional Group. Table 4 presents the enthalpies of reaction for a series of abstractions of hydrogens from nitrones, imines, aldehydes, and alkenes. The enthalpies were determined in all cases at the B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d) level and in some cases at the G2 level of theory. The reaction in question in each case is $X-H + CH_3^\bullet \rightarrow X^\bullet + CH_4$. Where *E* and *Z* starting materials or products potentially exist, only data for reactions of the more stable isomers are listed. In general, the variation between the B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d) and G2 results is from 2 to 15 kJ/mol, the former being more exothermic than the latter, in line with the test cases (Tables 1 and 2).

In the case of nitrone, $H_2C=N(O)H$, abstraction of the H bonded to the N is clearly favored over that of the H bonded to the C ($\Delta H_{rxn} = -144$ and 50 kJ/mol, respectively). Substituents on the C reduce the exothermicity of abstraction of the N−H only slightly (ΔH_{rxn} becomes −137 kJ/mol for $CH_3CH=N(O)H$ and −136 kJ/mol for $C_6H_5CH=N(O)H$). Substituents on the C reduce the endothermicity of abstraction of the C_1-H on the nitrone, but for all species examined, the abstraction remains endothermic ($\Delta H_{rxn} = 50$, 36, and 37 kJ/mol for $H_2C=N(O)H$, $CH_3CH=N(O)H$, and $C_6H_5CH=N(O)H$, respectively.) Substituents on the N similarly reduce the endothermicity of abstraction of the C_1-H ($\Delta H_{rxn} = 50$, 39, and 36 kJ/mol for $H_2C=N(O)H$, $H_2C=N(O)CH_3$, and $H_2C=N(O)C_6H_5$, respectively.) Substituents at both positions have an approximately additive effect, e.g., $\Delta H_{rxn} = 28$ kJ/mol for $CH_3CH=NCH_3$.

For methyl imine ($H_2C=NH$), as noted above in the discussion of the data in Table 2, abstraction of the N−H is also favored over that of the C−H ($\Delta H_{rxn} = -75$ vs −41 kJ/mol). The presence of a substituent on the carbon reduces the exothermicity of the abstraction of the N−H very slightly ($\Delta H_{rxn} = -75$ for $H_2C=NH$, −68 kJ/mol for $CH_3CH=NH$, and −60 kJ/mol for $C_6H_5CH=NH$), as also noted with the corresponding nitrone series. The exothermicity associated with abstraction of the C−H is also decreased when a substituent is on the nitrogen (ΔH_{rxn} is −41 kJ/mol for $CH_2=NH$, −38 kJ/mol for $CH_2=NCH_3$, and −37 kJ/mol for $CH_2=NC_6H_5$). That is, substitution on the β atom produces a slightly less negative reaction enthalpy for H abstraction.

For abstraction from aldehydes, substitution on the α atom decreases the exothermicity of the process ($\Delta H_{rxn} = -71$ kJ/mol for abstraction from $H_2C=O$, −68 kJ/mol for abstraction from $CH_3CH=O$, and −61 kJ/mol for abstraction from C_6H_5-$CH=O$).

TABLE 4: Reaction Enthalpies (kJ/mol) for Abstraction of $H^{\bullet}$ by CH_3

compound class	compound X−H	$X^{\bullet}$	ΔH_{rxn} (B3LYP)	ΔH_{rxn} (G2)
nitrones	$H_2C=N(O)H$	$H_2C=NO^{\bullet}$	−144	−129
	(*Z*) $CH_3CH=N(O)H$	$CH_3CH=NO^{\bullet}$	−137	
	(*Z*) $C_6H_5CH=N(O)H$	(*Z*) $C_6H_5CH=NO^{\bullet}$	−136	
	$H_2C=N(O)H$	(*Z*) $HC^{\bullet}=NOH$	50	56
	$H_2C=N(O)CH_3$	(*Z*) $HC^{\bullet}=N(O)CH_3$	39	
	$H_2C=N(O)C_6H_5$	(*Z*) $HC^{\bullet}=N(O)C_6H_5$	36	
	(*Z*) $CH_3CH=N(O)H$	(*Z*) $CH_3C^{\bullet}=N(O)H$	36	
	(*Z*) $CH_3CH=N(O)CH_3$	(*Z*) $CH_3C^{\bullet}=N(O)CH_3$	28	
	(*Z*) $C_6H_5CH=N(O)H$	(*Z*) $C_6H_5C^{\bullet}=NOH$	37	
	(*Z*) $C_6H_5CH=N(O)CH_3$	(*Z*) $C_6H_5C^{\bullet}=N(O)CH_3$	28	
	(*Z*) $C_6H_5CH=N(O)C(CH_3)_3$	(*Z*) $C_6H_5C^{\bullet}=N(O)C(CH_3)_3$	19	
	$H_2C=N(O)CH_3$	$H_2C=N(O)CH_2^{\bullet}$	−45	−34
	(*Z*) $CH_3CH=N(O)CH_3$	(*Z*) $CH_3CH=N(O)CH_2^{\bullet}$	−49	
	(*Z*) $C_6H_5CH=N(O)CH_3$	(*Z*) $C_6H_5CH=N(O)CH_2^{\bullet}$	−59	
	(*Z*) $C_6H_5CH=N(O)C(CH_3)_3$	(*Z*) $C_6H_5CH=N(O)C(CH_3)_2CH_2^{\bullet}$	−23	
	(*Z*) $CH_3CH=N(O)H$	(*Z*) $C^{\bullet}H_2CH=N(O)H$	−129	
	((*Z*)) $CH_3CH=N(O)CH_3$	(*Z*) $C^{\bullet}H_2CH=N(O)CH_3$	−125	
imines	$H_2C=NH$	$H_2C=N^{\bullet}$	−75	−69
	(*E*) $CH_3CH=NH$	$CH_3CH=N^{\bullet}$	−68	−65
	(*E*) $C_6H_5CH=NH$	$C_6H_5CH=N^{\bullet}$	−60	
	$H_2C=NH$	(*E*) $HC^{\bullet}=NH$	−41	−34
	$H_2C=NCH_3$	(*E*) $HC^{\bullet}=NCH_3$	−38	−28
	$H_2C=NC_6H_5$	(*E*) $HC^{\bullet}=NC_6H_5$	−37	
	(*E*) $CH_3CH=NH$	(*E*) $CH_3C^{\bullet}=NH$	−46	−40
	(*E*) $CH_3CH=NCH_3$	(*E*) $CH_3C^{\bullet}=NCH_3$	−40	
	(*E*) $CH_3CH=NC_6H_5$	(*E*) $CH_3C^{\bullet}=NC_6H_5$	−40	
	(*E*) $CH_3CH=NC_6H_5$	(*E*) $C^{\bullet}H_2CH=NC_6H_5$	−81	
	(*E*) $C_6H_5CH=NH$	(*E*) $C_6H_5C^{\bullet}=NH$	−40	
	(*E*) $C_6H_5CH=NCH_3$	(*E*) $C_6H_5C^{\bullet}=NCH_3$	−35	
	(*E*) $C_6H_5CH=NCH_2CH_2CH_3$	(*E*) $C_6H_5C^{\bullet}=NCH_2CH_2CH_3$	−35	
	(*E*) $C_6H_5CH=NC(CH_3)_3$	(*E*) $C_6H_5C^{\bullet}=NC(CH_3)_3$	−44	
	$H_2C=NCH_3$	$H_2C=NC^{\bullet}H_2$	−77	−65
	(*E*) $CH_3CH=NCH_3$	(*E*) $CH_3CH=NC^{\bullet}H_2$	−76	
	(*E*) $C_6H_5CH=NCH_3$	(*E*) $C_6H_5CH=NC^{\bullet}H_2$	−96	
	$H_2C=NCH_2CH_3$	$H_2C=NC^{\bullet}HCH_3$	−97	
	$H_2C=NCH_2CH_2CH_3$	$H_2C=NC^{\bullet}HCH_2CH_3$	−96	
	(*E*) $C_6H_5CH=NCH_2CH_2CH_3$	(*E*) $C_6H_5CH=NC^{\bullet}HCH_2CH_3$	−114	
	$H_2C=NCH_2CH_3$	$H_2C=NCH_2C^{\bullet}H_2$	−15	
	(*E*) $C_6H_5CH=NC(CH_3)_3$	$C_6H_5CH=N(CH_3)_2C^{\bullet}H_2$	−16	
	$H_2C=NCH_2CH_2CH_3$	$H_2C=NCH_2C^{\bullet}HCH_3$	−28	
	(*E*) $C_6H_5CH=NCH_2CH_2CH_3$	(*E*) $C_6H_5CH=NCH_2C^{\bullet}HCH_3$	−31	
	$H_2C=NCH_2CH_2CH_3$	$H_2C=NCH_2CH_2C^{\bullet}H_2$	−18	
	(*E*) $C_6H_5CH=NCH_2CH_2CH_3$	(*E*) $C_6H_5CH=NCH_2CH_2C^{\bullet}H_2$	−18	
	(*E*) $CH_3CH=NH$	(*E*) $C^{\bullet}H_2CH=NH$	−62	
	(*E*) $CH_3CH=NCH_3$	(*E*) $C^{\bullet}H_2CH=NCH_3$	−67	
	(*E*) $C_6H_5CH=NCH_3$	(*E*) $C_6H_4CH=NCH_3$	32, 38	
aldehydes	$H_2C=O$	$HC^{\bullet}=O$	−71	−69
	$CH_3CH=O$	$CH_3C^{\bullet}=O$	−68	−65
	$C_6H_5CH=O$	$C_6H_5C^{\bullet}=O$	−61	
	$CH_3CH=O$	$C^{\bullet}H_2C(H)=O$	−47	−37
alkenes	$H_2C=CH_2$	$H_2C=C^{\bullet}H$	22	26
	$CH_3CH=CH_2$	(*E*) $CH_3CH=C^{\bullet}H$	27	31
	$C_6H_5CH=CH_2$	(*E*) $C_6H_5CH=C^{\bullet}H$	24	
	$CH_3CH=CH_2$	$CH_3C^{\bullet}=CH_2$	5	14
	$C_6H_5CH=CH_2$	$C_6H_5C^{\bullet}=CH_2$	−21	
	(*E*) $CH_3CH=CHCH_3$	(*E*) $CH_3C^{\bullet}=CHCH_3$	8	
	$CH_3CH=CH_2$	$C^{\bullet}H_2C(H)=CH_2$	−80	−72

In the case of abstraction of H from alkenes, the abstraction of H from the functional group is endothermic in aliphatic alkenes, e.g., $\Delta H_{rxn} = 22$ kJ/mol for $H_2C=CH_2$. Methyl substitution on the α carbon makes the abstraction process less endothermic, whereas methyl substitution on the β carbon increases the endothermicity (for $H_3CCH=CH_2$, abstraction from the C_2 position has $\Delta H_{rxn} = 5$ kJ/mol, and from the C_1 position, $\Delta H_{rxn} = 27$ kJ/mol). Abstraction of a benzyllic H is exothermic ($\Delta H_{rxn} = -21$ kJ/mol in $C_6H_5CH=CH_2$) because of resonance stabilization.

Overall, comparison of the abstraction processes for H within the functional group suggests the relative likelihood of abstraction among the four types outlined in Scheme 3.

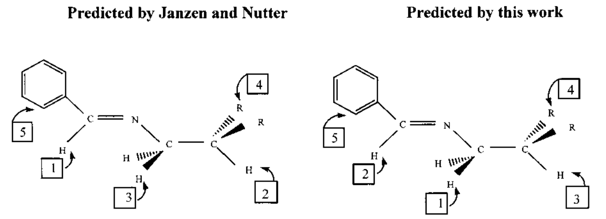
Substitution on the functional group affects the enthalpy of the abstraction process to some extent. For example, substitution on the C of nitrones and imines by methyl and phenyl groups decreases the exothermicity associated with the abstraction of the H on N.

Abstraction of $H^{\bullet}$ Distal to the Functional Group. In N-substituted nitrones, abstraction of an H from the *N*-methyl is exothermic (e.g., $\Delta H_{rxn} = -45$ kJ/mol for $H_2C=N(O)CH_3$) but considerably less so than abstraction of the N−H in $H_2C=N(O)H$ ($\Delta H_{rxn} = -144$ kJ/mol). On the other hand, abstraction of an H from the C_2 position in $CH_3CH=N(O)H$ ($\Delta H_{rxn} = -129$ kJ/mol) has an exothermicity approaching that of abstraction of the N−H in $H_2C=N(O)H$, because of

SCHEME 3

	nitrone	>	imine	≈	aldehyde	>	alkene.
	from N		from N		from C		from C
	$H_2C{=}N(O)H$		$H_2C{=}NH$		$H_2C{=}O$		$H_2C{=}CH_2$
ΔH_{rxn} =	−144 kJ/mol		−75 kJ/mol		−71 kJ/mol		22 kJ/mol

SCHEME 4



resonance stabilization of the resultant radical; this ΔH_{rxn} = −129 kJ/mol is a dramatic change relative to that for the abstraction of a C_1−H in the same compound, where ΔH_{rxn} = 36 kJ/mol.

For N-substituted imines, abstraction of the *N*-methyl-H (which we will refer to as the NC_1−H) has similar exothermicity to that of the N−H in the unsubstituted imine (e.g., for $H_2C{=}NC\mathbf{H}_3$, ΔH_{rxn} = −77 kJ/mol, whereas for $H_2C{=}N\mathbf{H}$, ΔH_{rxn} = −75 kJ/mol). Methyl substitution on the C has no effect (ΔH_{rxn} = −76 kJ/mol), but phenyl substitution on the C increases the exothermicity of the NC_1−H abstraction (ΔH_{rxn} = −96 kJ/mol for $C_6H_5CH{=}NC\mathbf{H}_3$), a resonance effect. Elongation of the N substituent also leads to a more exothermic abstraction process for the NC_1−H abstraction (ΔH_{rxn} = −97 kJ/mol for $H_2C{=}NC\mathbf{H}_2CH_3$), and when both C-phenyl substitution and elongation of the N substituent occur, the effect is essentially additive (ΔH_{rxn} = −114 kJ/mol for $C_6H_5CH{=}NC\mathbf{H}_2CH_2CH_3$). The further the H is from the N, the less favored the abstraction, e.g., for $C_6H_5CH{=}NCH_2CH_2CH_3$ as the starting material, abstraction of the NC_2−H and the NC_3−H have ΔH_{rxn} = −31 and −18 kJ/mol, respectively. Abstraction of H from the C_2 position in ethyl imine is preferred over abstraction from the C_1 position (ΔH_{rxn} = −62 vs −46 kJ/mol), but the change is not nearly as dramatic as the corresponding one in nitrones. Abstraction of any H on the aromatic ring of C-phenyl methyl imine is endothermic and, therefore, highly unfavored. These results suggest the order of preference for abstraction of H from imines as outlined in Scheme 4, which differs to some extent from the order predicted by Janzen and Nutter.[2]

Abstraction of the H at the C_2 position in ethanal is less favored than that of the H at the C_1 position (compare ΔH_{rxn} = −47 and −68 kJ/mol, respectively, for $CH_3CH{=}O$) which is surprising in view of the potential for resonance stabilization of the $^{\bullet}CH_2CH{=}O$ radical ($H_2^{\bullet}CCH{=}O \leftrightarrow H_2C{=}CHO^{\bullet}$).

Abstraction of H from the C_3 in propene ($C\mathbf{H}_3CH{=}CH_2$) is exothermic (ΔH_{rxn} = −80 kJ/mol) unlike that from the C_2 position (ΔH_{rxn} = 5 kJ/mol), because of resonance stabilization.

Addition of $CH_3^{\bullet}$ to the Functional Group. Table 5 presents the results of calculations of enthalpies of reaction for the reaction type $X{-}H + CH_3^{\bullet} \rightarrow CH_3{-}X^{\bullet}{-}H$.

Addition to nitrone is thermodynamically favored at the C position, relative to that at the O or N sites (ΔH_{rxn} = −185, −54, and 26 kJ/mol, respectively), as has been calculated previously[1] and observed experimentally.[14] Substitution at either the C or N position reduces the exothermicity slightly, but addition to the nitrone C still remains the thermodynamically preferred process even in the most substituted nitrone studied, $C_6H_5CH{=}N(O)CH_3$, where ΔH_{rxn} = −143 kJ/mol.

For imines, the site specificity is less evident, as noted in the discussion of the results in Table 1; thus, for addition to the C position in $H_2C{=}NH$, ΔH_{rxn} is −76 kJ/mol, whereas for addition to the N position, it is −79 kJ/mol. The effect of substitution on the addition to the C position will be considered first. Methyl and phenyl substitution at the N *increase* the exothermicity of addition to C (i.e., ΔH_{rxn} goes from −76 kJ/mol for $H_2C{=}NH$ to −89 kJ/mol for $H_2C{=}NCH_3$ and −122 kJ/mol for $H_2C{=}NC_6H_5$, which are changes in ΔH_{rxn} of −13 and −46 kJ/mol, respectively). On the other hand, methyl and phenyl substitution at the C *decrease* the exothermicity of addition to C (ΔH_{rxn} goes from −76 kJ/mol for $H_2C{=}NH$ to −54 kJ/mol for $CH_3CH{=}NH$ and −38 kJ/mol for $C_6H_5CH{=}NH$, increases in ΔH_{rxn} of 22 and of 38 kJ/mol, respectively). When substitution occurs at both the N and the C, as in $CH_3CH{=}NCH_3$, $C_6H_5CH{=}NCH_3$, and $CH_3CH{=}NC_6H_5$, the exothermicity-increasing effect of N substitution and the exothermicity-decreasing effect of C substitution are approximately additive.

Substitution on N slightly reduces the exothermicity associated with addition to the N position in imines (ΔH_{rxn} is −79 kJ/mol for $H_2C{=}NH$ and −71 kJ/mol for $H_2C{=}NCH_3$, a change in ΔH_{rxn} of 8 kJ/mol). Substitution on C also reduces the exothermicity (ΔH_{rxn} becomes −63 kJ/mol for $CH_3CH{=}NH$, a change in ΔH_{rxn} of 16 kJ/mol). Substituents at both positions again give an approximately additive effect, e.g., ΔH_{rxn} = −49 kJ/mol for addition to $CH_3CH{=}NCH_3$, a change of 30 kJ/mol. When a phenyl substitution is made at the C position, resonance allows the exothermicity to increase slightly (ΔH_{rxn} = −82 kJ/mol for $C_6H_5CH{=}NH$ for methyl addition to N).

Overall, addition to C is generally preferred over addition to N in substituted imines. However, this varies with the nature of the substituents. For example, when there is a methyl substituent on each of the C and the N, as in $CH_3CH{=}NCH_3$, addition to C is favored (ΔH_{rxn} = −62 kJ/mol for C addition vs −49 kJ/mol for N addition). Similarly, with a phenyl substituent on the N, as in $CH_3CH{=}NC_6H_5$, addition to C is favored (ΔH_{rxn} = −94 kJ/mol for C vs −46 kJ/mol for N). On the other hand, addition to N is favored in $C_6H_5CH{=}NCH_3$ (ΔH_{rxn} = −46 kJ/mol for C addition and −74 kJ/mol for N addition.) A phenyl substituent on the α atom hinders addition, whereas one on the β atom favors addition because of resonance stabilization.

Addition of the methyl radical to formaldehyde is more favorable at the carbon than at the oxygen; ΔH_{rxn} = −54 and −31 kJ/mol, respectively. Substitution on the C reduces the exothermicity of addition to the C; e.g., addition to $CH_3CH{=}O$ has ΔH_{rxn} = −16 kJ/mol, and addition to $C_6H_5CH{=}O$ has ΔH_{rxn} = −1 kJ/mol.

In the case of addition to $H_2C{=}CH_2$, ΔH_{rxn} is −86 kJ/mol. Substitution at the C to which the addition is occurring reduces the exothermicity; substitution at the other carbon either has no effect or, in the case of phenyl substitution, increases the exothermicity because of a resonance stabilization of the resultant radical (e.g., addition to the C_2 position in $C_6H_5CH{=}CH_2$ gives ΔH_{rxn} = −121 kJ/mol.)

Thus, the relative exothermicity for addition of the $CH_3^{\bullet}$ to the four functional groups is presented in Scheme 5. The comparison is made for comparably substituted compounds, as listed.

Addition vs Abstraction. Abstraction of the N−H from nitrones with no N substituent is only slightly less exothermic than addition to the same nitrones; for example, abstraction from $C_6H_5CH{=}N(O)H$ has ΔH_{rxn} = −136 kJ/mol, and addition to C of the same compound has ΔH_{rxn} = −145

TABLE 5: Reaction Enthalpies (kJ/mol) for Addition of CH_3

compound class	compound X−H	$CH_3-X^{\bullet}-H$	ΔH_{rxn} (B3LYP)	ΔH_{rxn} (G2)
nitrones	$H_2C{=}N(O)H$	$CH_3CH_2N(O^{\bullet})H$	−185	−189
	$H_2C{=}N(O)CH_3$	$CH_3CH_2N(O^{\bullet})CH_3$	−181	
	$H_2C{=}N(O)C_6H_5$	$CH_3CH_2N(O^{\bullet})C_6H_5$	−206	
	(*E*) $CH_3CH{=}N(O)H$	$(CH_3)_2CHN(O^{\bullet})H$	−176	
	(*Z*) $CH_3CH{=}N(O)CH_3$	$(CH_3)_2CHN(O^{\bullet})CH_3$	−154	
	(*Z*) $C_6H_5CH{=}N(O)H$	$C_6H_5(CH_3)CHN(O^{\bullet})H$	−145	
	(*Z*) $C_6H_5CH{=}N(O)CH_3$	$C_6H_5(CH_3)CHN(O^{\bullet})CH_3$	−143	
	$H_2C{=}N(O)H$	$H_2C^{\bullet}N(H)OCH_3$	−54	−59
	$H_2C{=}N(O)H$	$H_2C^{\bullet}N(O)HCH_3$	26	7
	(*Z*) $C_6H_5CH{=}N(O)H$	$C_6H_5C^{\bullet}HN(O)HCH_3$	26	
imines	$H_2C{=}NH$	$CH_3CH_2N^{\bullet}H$	−76	−78
	$H_2C{=}NCH_3$	$CH_3CH_2N^{\bullet}CH_3$	−89	
	$H_2C{=}NC_6H_5$	$CH_3CH_2N^{\bullet}C_6H_5$	−122	
	(*E*) $CH_3CH{=}NH$	$(CH_3)_2CHN^{\bullet}H$	−54	
	(*E*) $C_6H_5CH{=}NH$	$C_6H_5(CH_3)CHN^{\bullet}H$	−38	
	(*E*) $CH_3CH{=}NCH_3$	$(CH_3)_2CHN^{\bullet}CH_3$	−62	
	(*E*) $CH_3CH{=}NC_6H_5$	$(CH_3)_2CHN^{\bullet}C_6H_5$	−94	
	(*E*) $C_6H_5CH{=}NCH_3$	$C_6H_5(CH_3)CHN^{\bullet}CH_3$	−46	
	$H_2C{=}NCH_2CH_3$	$CH_3CH_2N^{\bullet}CH_2CH_3$	−90	
	(*E*) $C_6H_5CH{=}NC(CH_3)_3$	$C_6H_5(CH_3)CHN^{\bullet}C(CH_3)_3$	−40	
	$H_2C{=}NH$	$H_2C^{\bullet}N(H)CH_3$	−79	−78
	$H_2C{=}NCH_3$	$H_2C^{\bullet}N(CH_3)_2$	−71	
	$H_2C{=}NC_6H_5$	$H_2C^{\bullet}N(CH_3)C_6H_5$	−78	
	(*E*) $CH_3CH{=}NC_6H_5$	$CH_3C^{\bullet}HN(CH_3)C_6H_5$	−46	
	(*E*) $CH_3CH{=}NH$	$CH_3C^{\bullet}HN(H)CH_3$	−63	
	(*E*) $C_6H_5CH{=}NH$	$C_6H_5C^{\bullet}HNHCH_3$	−82	
	(*E*) $CH_3CH{=}NCH_3$	$CH_3C^{\bullet}HN(CH_3)_2$	−49	
	(*E*) $C_6H_5CH{=}NCH_3$	$C_6H_5C^{\bullet}HN(CH_3)_2$	−74	
	(*E*) $C_6H_5CH{=}NC(CH_3)_3$	$C_6H_5C^{\bullet}HN(CH_3)C(CH_3)_3$	−58	
aldehydes	$H_2C{=}O$	$CH_3CH_2O^{\bullet}$	−54	−40
	$H_2C{=}O$	$H_2C^{\bullet}OCH_3$	−31	−32
	$CH_3CH{=}O$	$(CH_3)_2CHO^{\bullet}$	−16	
	$CH_3CH{=}O$	$CH_3C^{\bullet}HOCH_3$	−12	
	$C_6H_5CH{=}O$	$C_6H_5(CH_3)CHO^{\bullet}$	−1	
	$C_6H_5CH{=}O$	$C_6H_5C^{\bullet}HOCH_3$	−48	
alkenes	$H_2C{=}CH_2$	$CH_3CH_2C^{\bullet}H_2$	−86	−94
	$CH_3CH{=}CH_2$	$(CH_3)_2CHC^{\bullet}H_2$	−73	
	$C_6H_5CH{=}CH_2$	$C_6H_5(CH_3)CHC^{\bullet}H_2$	−60	
	$CH_3CH{=}CH_2$	$CH_3C^{\bullet}HCH_2CH_3$	−86	
	$C_6H_5CH{=}CH_2$	$C_6H_5C^{\bullet}HCH_2CH_3$	−121	
	$CH_3CH{=}CHCH_3$	$(CH_3)_2CHC^{\bullet}HCH_3$	−72	

SCHEME 5

nitrone	>	alkene	>	imine	>	aldehyde
to C		to C_2		to N		to C
in		in		in		in
$C_6H_5CH{=}N(O)CH_3$		$C_6H_5CH{=}CH_2$		$C_6H_5CH{=}NCH_3$		$C_6H_5CH{=}O$
$\Delta H_{rxn} = -143$ kJ/mol		−121 kJ/mol		−74 kJ/mol		−1 kJ/mol

kJ/mol. However, once there is an N substituent so that N−H abstraction is no longer an option, there is an enormous difference between enthalpies of abstraction and addition. For example, with $C_6H_5CH{=}N(O)CH_3$, abstraction of the C_1−H has $\Delta H_{rxn} = 28$ kJ/mol and abstraction of the NC_1−H has $\Delta H_{rxn} = -59$ kJ/mol; on the other hand, addition to the C_1 position has $\Delta H_{rxn} = -143$ kJ/mol. Thus, addition is predicted by the computations in this study to be strongly favored over abstraction for nitrones. This is not surprising in view of the extensive literature on the use of nitrones as spin traps.[15]

Alkenes are also known experimentally to prefer addition over abstraction,[5] a fact which is supported by these calculations. Abstractions from the C_1 and C_2 positions of $C_6H_5CH{=}CH_2$ have $\Delta H_{rxn} = -21$ and 24 kJ/mol, respectively. These are much less favorable than the additions to the C_1 and C_2 positions, which have $\Delta H_{rxn} = -60$ and −121 kJ/mol, respectively.

By contrast, aldehydes undergo abstraction more readily than addition. For benzaldehyde, $C_6H_5CH{=}O$, abstraction of the C_1−H has $\Delta H_{rxn} = -61$ kJ/mol, whereas addition to the C_1 position has $\Delta H_{rxn} = -1$ kJ/mol. Addition to the O is more favored than addition to C_1 ($\Delta H_{rxn} = -48$ kJ/mol) but is still less favored than abstraction of the C_1−H.

The calculated enthalpies of reaction suggest that imines which have a NC_1−H favor abstraction over addition; however, in the absence of an NC_1−H, addition becomes the preferred route, and the nature of the substituent affects the preferred site of addition. Consider N-benzylidenemethylamine, $C_6H_5CH{=}NCH_3$. Abstraction of the C_1−H ($\Delta H_{rxn} = -35$ kJ/mol) is definitely not favored relative to that of the NC_1−H ($\Delta H_{rxn} = -96$ kJ/mol). The latter is favored over addition to the N ($\Delta H_{rxn} = -74$ kJ/mol), which in turn is preferred to addition to the C ($\Delta H_{rxn} = -46$ kJ/mol). Thus, for $C_6H_5CH{=}NCH_3$, abstraction of the NC_1−H is the favored process. On the other hand, when the NC_1 position is fully substituted, as in $C_6H_5CH{=}NC(CH_3)_3$, obviously there is now no NC_1−H to abstract, so the most exothermic abstraction is that of the C_1−H, which has $\Delta H_{rxn} = -44$ kJ/mol. Addition to the C position is not greatly affected by the N-*tert*-butyl group (ΔH_{rxn} is −46 kJ/mol when the N substituent is a methyl group and −40 kJ/mol when the N substituent is a *t*-butyl group). Addition to the N position ($\Delta H_{rxn} = -58$ kJ/mol) is less favored with the N-*tert*-butyl substituent than with the *N*-methyl one ($\Delta H_{rxn} = -74$ kJ/mol) because of steric hindrance, but overall addition to the N is the preferred process for

TABLE 6: Reaction and Activation Enthalpies (kJ/mol) for Abstraction of $H^{\bullet}$ by CH_3 $X{-}H + CH_3^{\bullet} \rightarrow X^{\bullet} + CH_4$

compound class	compound X−H	product $X^{\bullet}$	TS dipole moment (D)	B3LYP		G2	
				ΔH_{rxn}	$\Delta H^{\ddagger}$	ΔH_{rxn}	$\Delta H^{\ddagger}$
nitrones	$H_2C{=}N(O)H$	$H_2C{=}NO^{\bullet}$	3.21	−144	−5	−129	7
	$H_2C{=}N(O)H$	$HC^{\bullet}{=}N(O)H$ (*Z*)	3.81	50	53	56	85
	$H_2C{=}N(O)H$	$HC^{\bullet}{=}N(O)H$ (*E*)	3.13	58	69	68	85
	(*Z*) $CH_3CH{=}N(O)CH_3$	(*Z*) $CH_3C^{\bullet}{=}N(O)CH_3$	3.56	28	66		
	$H_2C{=}N(O)CH_3$	$H_2C{=}N(O)CH_2^{\bullet}$	3.46	−45	42	−34	
	(*Z*) $CH_3CH{=}N(O)CH_3$	$^{\bullet}CH_2CH{=}N(O)CH_3$	3.22	−125	25		
imines	$H_2C{=}NH$	$H_2C{=}N^{\bullet}$	1.87	−75	16	−69	31
	$H_2C{=}NH$	(*Z*) $HC^{\bullet}{=}NH$	1.81	−24	43	−15	61
	$H_2C{=}NH$	(*E*) $HC^{\bullet}{=}NH$	1.44	−41	34	−34	51
	(*E*) $CH_3CH{=}NCH_3$	(*E*) $CH_3C^{\bullet}{=}NCH_3$	0.7	−40	36		
	(*E*) $C_6H_5CH{=}NCH_3$	(*E*) $C_6H_5C^{\bullet}{=}NCH_3$	0.54	−35	43		
	$H_2C{=}NCH_3$	$H_2C{=}NCH_2^{\bullet}$	1.42	−77	36	−65	
	(*E*) $CH_3CH{=}NCH_3$	(*E*) $CH_3CH{=}NCH_2^{\bullet}$	1.34	−76	37		
aldehydes	$H_2C{=}O$	$HC^{\bullet}{=}O$	1.85	−71	21	−69	37
	$CH_3HC{=}O$	$CH_3C^{\bullet}{=}O$	2.4	−68	23		
alkenes	$H_2C{=}CH_2$	$HC^{\bullet}{=}CH_2$	0.05	22	62	26	75
	$CH_3(H)C{=}CH_2$	$CH_3C^{\bullet}{=}CH_2$	0.46	5	52	14	
	(*E*) $CH_3(H)C{=}CHCH_3$	(*E*) $CH_3C^{\bullet}{=}CHCH_3$	0.19	8	58		
	$CH_3(H)C{=}CH_2$	$C^{\bullet}H_2(H)C{=}CH_2$	0.33	−80	36		

TABLE 7: Reaction and Activation Enthalpies (kJ/mol) for Addition of $CH_3^{\bullet}$ $CH_3^{\bullet} + X{-}H \rightarrow CH_3{-}X^{\bullet}{-}H$

compound class	compound X−H	product $CH_3{-}X{-}H$	TS dipole moment (D)	B3LYP		G2	
				ΔH_{rxn}	$\Delta H^{\ddagger}$	ΔH_{rxn}	$\Delta H^{\ddagger}$
nitrones	$H_2C{=}N(O)H$	$CH_3CH_2N(O^{\bullet})H$	3.37	−185	7	−189	10
	$H_2C{=}N(O)CH_3$	$CH_3CH_2N(O^{\bullet})CH_3$	3.45	−181	8		
	(*Z*) $CH_3CH{=}N(O)CH_3$	$(CH_3)_2CHN(O^{\bullet})CH_3$	3.26	−154	13		
	$H_2C{=}N(O)H$	$H_2C^{\bullet}N(H)OCH_3$	2.42	−54	41	−59	60
	$H_2C{=}N(O)H$	$H_2C^{\bullet}N(O)(H)CH_3$	3.68	26	94	7	97
imines	$H_2C{=}NH$	$CH_3CH_2N^{\bullet}H$	2.22	−76	27	−78	32
	$H_2C{=}NCH_3$	$CH_3CH_2N^{\bullet}CH_3$	1.63	−89	26		
	(*E*) $CH_3CH{=}NCH_3$	$(CH_3)_2CHN^{\bullet}CH_3$	1.5	−62	40		
	(*E*) $C_6H_5CH{=}NCH_3$	$C_6H_5(CH_3)CHN^{\bullet}CH_3$	1.04	−46	42		
	$H_2C{=}NH$	$H_2C^{\bullet}N(H)CH_3$	1.39	−79	40	−78	50
	(*E*) $CH_3CH{=}NCH_3$	$CH_3C^{\bullet}HN(CH_3)_2$	0.95	−49	57		
	(*E*) $CH_3CH{=}NC_6H_5$	$(CH_3)_2CHN^{\bullet}C_6H_5$	1.56	−94	33		
	(*E*) $C_6H_5CH{=}NCH_3$	$C_6H_5C^{\bullet}HN(CH_3)_2$	0.8	−74	45		
aldehydes	$H_2C{=}O$	$CH_3CH_2O^{\bullet}$	2.78	−54	19	−40	27
	$CH_3HC{=}O$	$(CH_3)_2HCO^{\bullet}$	2.75	−16	37		
	$H_2C{=}O$	$H_2C^{\bullet}OCH_3$	1.43	−31	61	−32	80
alkenes	$H_2C{=}CH_2$	$CH_3CH_2C^{\bullet}H_2$	0.19	−86	30	−94	33
	$CH_3HC{=}CH_2$	$(CH_3)_2HCC^{\bullet}H_2$	0.32	−73	41		
	(*E*) $CH_3CH{=}CHCH_3$	$(CH_3)_2HCC^{\bullet}HCH_3$	0.21	−72	40		
	$CH_3HC{=}CH_2$	$CH_3C^{\bullet}HCH_2CH_3$	0.23	−86	30		

$C_6H_5CH{=}NC(CH_3)_3$. With $CH_3CH{=}NC_6H_5$, addition to C becomes the favored process. (Abstraction of the $C_1{-}H$ gives $\Delta H_{rxn} = -40$ kJ/mol; abstraction of the $C_2{-}H$ has $\Delta H_{rxn} = -81$ kJ/mol; addition to the N has $\Delta H_{rxn} = -46$ kJ/mol; addition to the C has $\Delta H_{rxn} = -94$ kJ/mol.) These data suggest that N-substituted imines can trap radicals at either C or N depending on the substituent present.

Transition State Enthalpies. On the basis of the above computationally predicted thermodynamic data, the preference for abstraction vs addition is not clear-cut with imines. Therefore, a study of the transition state structures for addition and abstraction processes was undertaken to see if addition or abstraction is preferred for kinetic reasons. For comparison, a similar study was done for all four functional groups. The data for the abstraction processes are given in Table 6, and those for the addition processes are in Table 7.

The nitrone data again support the fact that addition is the preferred process for this class of compounds. Among the possible abstractions, that of the N−H in the unsubstituted nitrone is the most favored both thermodynamically and kinetically. In fact, this reaction appears to have a negative activation enthalpy. (This may be an artifact due to the fact that the energy calculation is a single point one, at a transition state geometry optimized with a smaller basis set. Furthermore, there may be a reaction complex of lower energy than the two separate starting materials.[16,17] No attempt was made to find a reaction complex.) Although not negative, the actual activation energy is undoubtedly very low. Abstractions from the C position have much higher enthalpies of activation as well as being endothermic processes overall, and are clearly less favored. In substituted nitrones, such as $CH_3CH{=}N(O)CH_3$, abstraction from the NC_1 position gives a moderately high $\Delta H^{\ddagger}$ of 42 kJ/mol and a ΔH_{rxn} of −45 kJ/mol. Abstraction from the C_2 position is more favored than that from the NC_1, with $\Delta H^{\ddagger} = 25$ kJ/mol and $\Delta H_{rxn} = -125$ kJ/mol, because of greater resonance stabilization. Of course, in commonly used nitrone spin traps, there is no $C_2{-}H$ available (e.g., PBN, DMPO, and 4-POBN),[18] so the possibility of abstraction from this position is removed.

By comparison, the addition reactions for nitrones all have very low $\Delta H^{\ddagger}$ as well as being highly exothermic overall; for example, $\Delta H^{\ddagger} = 7$ kJ/mol with $\Delta H_{rxn} = -185$ kJ/mol for addition to C in $H_2C{=}N(O)H$, and $\Delta H^{\ddagger} = 13$ with $\Delta H_{rxn} = -154$ kJ/mol for addition to the C_1 in the substituted species $CH_3CH{=}N(O)CH_3$. The substituted nitrone therefore adds the methyl radical with a lower enthalpy of activation, and the overall reaction is more exothermic than any abstraction processes from the same molecule.

Abstractions of H from alkenes have higher activation enthalpies and are less exothermic than additions to the same species. For example, abstraction of a $C_2{-}H$ in $CH_3HC{=}CHCH_3$ has $\Delta H^{\ddagger} = 58$ kJ/mol and $\Delta H_{rxn} = 8$ kJ/mol; addition to a C_2 position has $\Delta H^{\ddagger} = 40$ kJ/mol and $\Delta H_{rxn} = -72$ kJ/mol. Even the abstraction process which is most favored among the ones studied, i.e., that of abstraction of the $C_3{-}H$ from $CH_3CH{=}CH_2$, which has $\Delta H^{\ddagger} = 36$ kJ/mol and $\Delta H_{rxn} = -80$ kJ/mol, is less favored than addition to the same molecule, which has $\Delta H^{\ddagger} =$ 30 kJ/mol and $\Delta H_{rxn} = -86$ kJ/mol. Addition is therefore both thermodynamically and kinetically favored over abstraction in alkenes.

For aldehydes, the abstraction process is the preferred one, both thermodynamically and kinetically. For example, with $CH_3CH{=}O$, abstraction of the $C_1{-}H$ has $\Delta H^{\ddagger} = 23$ kJ/mol and $\Delta H_{rxn} = -68$ kJ/mol, whereas addition to the C_1 position has $\Delta H^{\ddagger} = 37$ kJ/mol and $\Delta H_{rxn} = -16$ kJ/mol.

With the simple imine, $CH_2{=}NH$, kinetic arguments suggest that abstraction of the N−H is favored by about 11 kJ/mol over addition to C; thermodynamically the two processes are identical. (Abstraction of the N−H has $\Delta H^{\ddagger} = 16$ kJ/mol and ΔH_{rxn} $= -75$ kJ/mol, whereas addition to the C has $\Delta H^{\ddagger} = 27$ kJ/mol and $\Delta H_{rxn} = -76$ kJ/mol.)

With the substituted imine $CH_3CH{=}NCH_3$, addition to C_1 gives $\Delta H^{\ddagger} = 40$ kJ/mol and $\Delta H_{rxn} = -62$ kJ/mol, whereas addition to N yields $\Delta H^{\ddagger} = 57$ kJ/mol and $\Delta H_{rxn} = -49$ kJ/mol. Abstraction of the $C_1{-}H$ has $\Delta H^{\ddagger} = 36$ kJ/mol and $\Delta H_{rxn} = -40$ kJ/mol, with abstraction of the $NC_1{-}H$ having $\Delta H^{\ddagger} = 37$ kJ/mol and the $\Delta H_{rxn} = -76$ kJ/mol. Thus, the two abstraction processes are calculated to have indistinguishable $\Delta H^{\ddagger}$. Abstraction of the $NC_1{-}H$ therefore appears to be the favored process for $CH_3CH{=}NCH_3$ for thermodynamic reasons.

In $CH_3CH{=}NC_6H_5$, addition to C_1 has $\Delta H^{\ddagger} = 33$ kJ/mol and $\Delta H_{rxn} = -94$ kJ/mol; the N-phenyl substituent lowers the activation energy slightly and stabilizes the adduct quite significantly. The N-phenyl substituent in $CH_3CH{=}NC_6H_5$ does not change the ΔH_{rxn} for abstraction of the $C_1{-}H$ relative to that for the *N*-methyl substituent, with ΔH_{rxn} being −40 kJ/mol for both, so $\Delta H^{\ddagger}$ for $CH_3CH{=}NC_6H_5$ was not separately determined but is probably about 36 kJ/mol. For $CH_3CH{=}NC_6H_5$, therefore, addition to the C_1 is strongly favored thermodynamically (and probably slightly favored kinetically) relative to abstraction.

For N-benzylidenemethylamine, $C_6H_5CH{=}NCH_3$, addition to N gives $\Delta H^{\ddagger} = 45$ kJ/mol and $\Delta H_{rxn} = -74$ kJ/mol. Addition to C_1 has $\Delta H^{\ddagger} = 42$ kJ/mol and $\Delta H_{rxn} = -46$ kJ/mol. Abstraction of the $C_1{-}H$ yields $\Delta H^{\ddagger} = 43$ kJ/mol and $\Delta H_{rxn} =$ -35 kJ/mol. The differences in the calculated activation enthalpies are not significant enough to draw any conclusions about whether abstraction is kinetically favored relative to addition. Thermodynamically, addition to N is the preferred process, with addition to C_1 the second most likely result; abstraction, although slightly favored kinetically over addition to N, is the least likely process thermodynamically. This is not the anticipated result, in view of the experimental data reported by Janzen and Nutter[2] which give no evidence for addition of the *t*-butoxyl radical to benzylideneamines; only hydrogen abstraction by this radical was found. The use of the *t*-butoxyl radical, rather than the methyl radical, may be a factor causing different results for the experimental compared to the theoretical study: the *t*-butoxyl radical is oxygen-centered and is bulkier, so it may add less readily than the small carbon-centered methyl radical. (A theoretical study of the how the nature of the radical influences whether addition or abstraction occurs with imines is currently underway.) The reactions of Janzen and Nutter were run in benzene, whereas the theoretical calculations involve "gas phase" reactions, but the effect of nonpolar solvents is known to be small and so is unlikely to be a cause for the different reactivities observed experimentally and theoretically. (For example, relative to the gas-phase results for radical addition to alkenes, the activation energy barrier varies by ±1 kJ/mol for solvents with dielectric constant of 2).[19] Janzen and Nutter report that the abstraction of the iminyl hydrogen atom, $-C\mathbf{H}{=}N-$ (with absolute rate constant = 1.2 × 10^4 M^{-1} s^{-1}) was "considerably slower" than that for benzaldehyde (with absolute rate constant = 2.4 × 10^7 M^{-1} s^{-1}), i.e., their results indicate that imines are less prone to abstraction than aldehydes, which is certainly predicted by our data. Both experiment and theory then suggest that imines hover on the dividing line between preference for addition vs abstraction.

TABLE 8: Bond Lengths (Å) at the Transition State (B3LYP/6-31G(d) Optimized Geometry)

	Abstraction of **H** by $CH_3^{\bullet}$				Addition of $CH_3^{\bullet}$ to **C**	
compound	ΔH_{rxn}	C−**H**	**H**−CH_3	C−**H**−CH_3	ΔH_{rxn}	**C**−CH_3
$H_2\mathbf{C}{=}N(O)C\mathbf{H}_3$	−45	1.309	1.390	2.697	−181	2.720
$\mathbf{H}_2C{=}N(O)H$	+50	1.414	1.273	2.687		
$CH_3\mathbf{CH}{=}N(O)CH_3$	+28	1.376	1.312	2.686	−154	2.645
$C\mathbf{H}_3HC{=}N(O)CH_3$	−125	1.232	1.551	2.781		
$\mathbf{H}_2\mathbf{C}{=}NH$	−41	1.295	1.435	2.730	−76	2.311
$H_2\mathbf{C}{=}NC\mathbf{H}_3$	−77	1.268	1.460	2.729	−89	2.329
$CH_3\mathbf{CH}{=}NCH_3$	−40	1.300	1.456	2.755	−62	2.283
$C_6H_5\mathbf{CH}{=}NCH_3$	−35	1.311	1.557	2.758	−46	2.247
$CH_3\mathbf{C}H{=}NC_6H_5$					−94	2.383
$\mathbf{H}_2\mathbf{C}{=}O$	−71	1.268	1.503	2.770	−54	2.250
$CH_3\mathbf{CH}{=}O$	−68	1.269	1.512	2.781	−16	2.182
$C\mathbf{H}_3CH{=}\mathbf{C}H_2$	−80	1.267	1.476	2.742	−86	2.365
$CH_3C\mathbf{H}{=}\mathbf{C}HCH_3$	+8	1.346	1.353	2.698	−72	2.333

Polarities and Bond Lengths at the Transition State. Tables 6 and 7 give the dipole moments of the transition state structures. Janzen and Nutter have suggested that the transition states for the classes of compound which tend to undergo addition might be more polar than those which undergo abstraction,[2] but we have no evidence to support this hypothesis. Alkenes, which favor addition, have transition-state structures with low polarity as one would expect, and nitrones, which also prefer addition, have highly polar transition-state structures. Imines and aldehydes are intermediate.

Bond lengths at the transition state are given in Table 8. Nitrones and alkenes, which undergo addition rather than abstraction, exhibit a longer $C{-}CH_3$ distance at the transition state for the addition process (about 2.7 and 2.35 Å, respectively) than do imines (about 2.3 Å) or aldehydes (about 2.2 Å). The $C{-}CH_3$ distance is particularly long for the nitrones. In accord with the Leffler-Hammond postulate,[20,21] the transition state for a substance which favors addition is more like the starting materials; the adding radical does not need to approach as closely to the C to which it will add when addition is the preferred route. Reactant-like character of the transition states for addition of the methyl radical to ethene and formaldehyde has also been reported by Gonzalez et al.[22] Furthermore, there is clearly a correlation between the $C{-}CH_3$ distance at the transition state and the exothermicity of the addition process for all of the compounds listed: the more exothermic the reaction, the further the adding methyl is from the C to which it adds. This is illustrated in Figure 1.

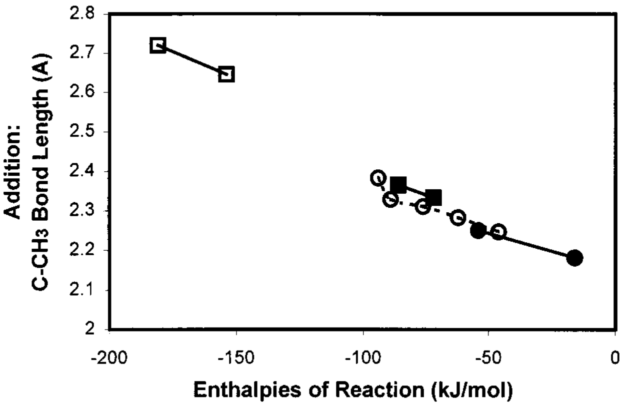


Figure 1. C−CH_3 bond lengths (Å) as a function of ΔH_{rxn} (kJ/mol) for addition of the methyl radical to the unsaturated C in nitrones, RCH=N(O)R′ (−□−); imines, R**C**H=NR′ (- -○- -); aldehydes, R**C**H=O (−●−); and alkenes, R**C**H=CHR′ (−■−).

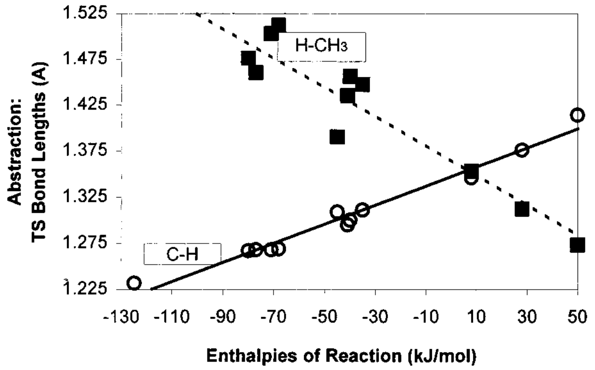


Figure 2. C−H (−○−) and H−CH_3 (- -■- -) bond lengths (Å) as a function of ΔH_{rxn} (kJ/mol) for abstraction of H from nitrones, imines, aldehydes, and alkenes.

For all of the abstraction processes the C−H−CH_3 distances at the transitions states are remarkably consistent at about 2.7 Å. The more exothermic the reaction, the shorter the C−H bond lengths at the transition state and the longer the H−CH_3 distances (Figure 2). Thus, again, the transition state structures are more like the starting materials when the processes are exothermic. Furthermore, when abstracting an H which is part of the functional group, as in RC**H**=N(O)R, RC**H**=NR, RC**H**=O, and RC**H**=CR_2, the transition structures for the aldehydes have the shortest C−H bond (1.27 Å) followed by those for the imines (1.3 Å), the alkenes (1.35 Å), and the nitrones (1.39 Å).

Thus, by bond length criteria as well as thermodynamic and kinetic criteria, imines are intermediate between aldehydes and alkenes in terms of their preference for abstraction or addition.

Conclusions

1. *Nitrones*. In the unsubstituted nitrone (H_2C=N(O)H), the most favorable H abstraction is that of the N−H; substituents on the C reduce the exothermicity slightly. Substituents on the N of course preclude abstraction of the N−H, and abstraction of the C_1−H is an endothermic process. Abstraction of the C_2−H from CH_3CH=N(O)CH_3 is exothermic, but experimentally used nitrones lack a C_2−H, e.g., PBN, C_6H_5CH=N(O)-C$(CH_3)_3$. Addition to the C_1 position in nitrones is strongly favored over abstraction, both kinetically and thermodynamically. Our calculations therefore confirm that nitrones experience addition of the methyl radical rather than abstractions of H by the radical.[2]

2. *Alkenes*. Abstraction of an H from H_2C=CH_2 is endothermic. If the abstracted H is benzyllic (as with the C_1−H in C_6H_5CH=CH_2), the process becomes exothermic. Also, when a C_3−H can be abstracted, as from CH_3CH=CH_2, the reaction is exothermic. However, addition of the methyl radical is a *more* exothermic reaction in all species studied and is therefore the favored route. The activation energy barriers are in reasonable agreement with those reported in an exhaustive and higher level theoretical study of radical addition to alkenes.[24]

3. *Aldehydes*. Abstraction of H from H_2C=O is exothermic. Substitution decreases the exothermicity of the abstraction process slightly. Addition is less favored than abstraction, particularly for substituted compounds. Aldehydes therefore experience abstraction in the presence of a methyl radical.[4,25]

4. *Imines*. Imines do not behave in as consistent a manner as the other types of compounds studied. Either addition or abstraction can be the favored process, depending on the substituents present. In H_2C=NH, abstraction of the N−H is somewhat favored because of a lower activation energy. In CH_3CH=NCH_3, abstraction of the NC_1−H is the preferred process. In CH_3CH=NC_6H_5, addition to C_1 is strongly favored thermodynamically and slightly favored kinetically. In N-benzylidenemethylamine, C_6H_5CH=NCH_3, addition to N is clearly the thermodynamically favored process, although kinetically the preference is very slightly in favor of abstraction of the C_1−H. The calculations therefore suggest that any preference for abstraction over addition for imines depends on the actual starting material. No broad generalization can be made. Whether the nature of the adding/abstracting radical has an influence is currently being investigated.

Acknowledgment. The financial support of the Mount Saint Vincent University Research Fund (to S.L.B.) and the Natural Sciences and Engineering Research Council of Canada (to R.J.B.) is gratefully acknowledged. We thank Professor Leo Radom and the Research School of Chemistry, Australian National University, for their gracious hospitality and computer time during the sabbaticals of S.L.B. and R.J.B.

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