Absolute Rate Constants for the Addition of Malonyl Radicals to Alkenes in Solution

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Absolute rate constants and their *Arrhenius* parameters are obtained for the addition of a cyclic malonyl radical derived from *Meldrum*'s acid to 20 mono- or 1,1-disubstituted alkenes in (±)-propylene oxide and for the addition of the open-chain di(*tert*-butyl)malonyl radical to six mono- or 1,1-disubstituted alkenes in 1,1,2-trichloro-1,2,2-trifluoroethane by time-resolved electron spin resonance spectroscopy. At room temperature, the radicals add at the unsubstituted C-atoms with rate constants ranging from $1.1 \cdot 10^5$ $M^{-1}s^{-1}$ (acrolein) to $2.4 \cdot 10^6$ $M^{-1}s^{-1}$ (1,1-diphenylethene). The frequency factors are in the narrow ranges of $\log (A/M^{-1}s^{-1}) = 8.7 \pm 0.1$ for the cyclic and $\log (A/M^{-1}s^{-1}) = 8.2 \pm 0.2$ for the open-chain malonyl species, whereas the activation energies vary from 12.9 kJ/mol (1,1-diphenylethene) to 21.7 kJ/mol (acrylonitrile). They correlate with the alkene ionization potentials and, more weakly, with the reaction enthalpy. No correlation was found between the activation energies and the alkene electron affinities. Hence, the results confirm and quantify the electrophilic nature of malonyl radicals in addition reactions.
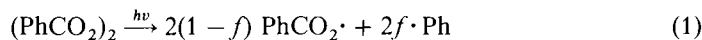
1. Introduction. – Additions of C-centered radicals to C=C bonds are amongst the most important free radical reactions and have many synthetic applications [1]. With radical and substrate, their rate constants vary by many orders of magnitude and reflect a complex interplay of polar, steric, and enthalpic substituent effects [2]. A separation of these effects requires the availability of large series of rate data and their activation parameters. To achieve this, we have measured rate constants and their temperature dependence for the addition of several C-centered radicals to a large variety of mono- and 1,1-disubstituted alkenes by time-resolved electron spin resonance (ESR) in liquid solution [3]. A comprehensive analysis [4] indicates that, for all radicals, the rate constants increase, and the barriers decrease with increasing reaction exothermicity in the sense of the *Evans-Polanyi* relation, but the behavior of the individual radicals is strongly modulated by polar alkene substituent effects. Thus, the easily oxidizable radicals *tert*-butyl ($(CH_3)_3\dot{C}$) [3a–c], hydroxymethyl ($\dot{C}H_2OH$) [3d], and 2-hydroxy-2-propyl ($(CH_3)_2\dot{C}OH$) [3e–g] show a strong nucleophilicity which obscures the enthalpy factor. Additions of the 2-cyano-2-propyl $(CH_3)_2\dot{C}CN$ [3h], the methyl ($\dot{C}H_3$) [3i], the benzyl ($Ph\dot{C}H_2$), and the cumyl radical [3k–m] follow the reaction enthalpy order more closely with only weak nucleophilic effects, and enthalpic effects also dominate the additions of cyanomethyl ($\dot{C}H_2CN$) and (*tert*-butoxy)carbonylmethyl ($\dot{C}H_2CO_2C(CH_3)_3$) radicals [3o, p], but for these a rate enhancement by electrophilic polar effects was also noticed.

So far, our studies have not included a radical with a dominant electrophilic addition behavior as it is known for the perfluoromethyl ($\dot{C}F_3$), the perfluoroalkyl ($C_nF_{2n+1}\dot{C}F_2$; $n = 1, 2, 6$), the perfluoro(*tert*-butyl) ($(CF_3)_3\dot{C}$) [5], and the dicyanomethyl ($H\dot{C}(CN)_2$) [6] radicals. Electrophilic properties have also been inferred for malonyl species $H\dot{C}(COOR)_2$ [7–9]. Moreover, we have studied hitherto only primary and tertiary alkyl

radicals, and an extension to secondary radicals seems appropriate. Hence, we have decided to determine now absolute rate constants and their *Arrhenius* parameters for the addition of two malonyl radicals, the cyclic 2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl radical (**1**; derived from *Meldrum*'s acid) adding to 20 alkenes in (±)-propylene oxide and the open-chain 2,2,8,8-tetramethyl-4,6-dioxo-3,7-dioxanon-5-yl (di(*tert*-butyl)-malonyl) radical to six alkenes in 1,1,2-trichloro-1,2,2-trifluoroethane (*Frigen 113*). The choice of radicals and solvents was, in part, determined by the ease of radical generation, but it should be noticed that the reactivity of malonyl-type radicals is also important for the understanding of some aspects of oscillating chemical reactions [10].

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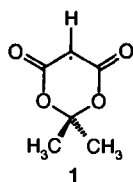
2. Methods and Results. – The arrangements and procedures for steady-state and time-resolved ESR have been described in detail in our earlier work [3][4]. The cyclic malonyl radical was generated by photolysis of 0.030M dibenzoyl peroxide (*Aldrich*; $\varepsilon \approx 1000$ $M^{-1}cm^{-1}$ at $\lambda \approx 280$ nm) in (±)-propylene oxide (*Fluka*, > 99.5%) containing 1.5M 2,2-dimethyl-1,3-dioxane-4,6-dione (*Meldrum*'s acid, *Aldrich*; repeatedly recrystallized following [11]).

$$(PhCO_2)_2 \xrightarrow{h\nu} 2(1-f)\ PhCO_2\cdot + 2f\cdot Ph \tag{1}$$

$$PhCO_2\cdot \longrightarrow \cdot Ph + CO_2 \tag{2}$$

$$\cdot Ph + RH \longrightarrow PhH + R\cdot \tag{3}$$

At room temperature, the fraction of multibond cleavage is $f \approx 0.29$, the $PhCO_2\cdot$ radical undergoes fragmentation (*Eqn. 2*) within *ca.* 200 ns [12], and the H-abstraction (*Eqn. 3*) is sufficiently fast for the chosen high substrate concentration and was not resolved in time with our technique. In steady-state photolysis, the cyclic malonyl radical (g = 2.0043, $a(1H_\alpha) = 19.35$ G, $a(6H_\varepsilon) = 0.18$ G at 298 K, see inset of *Fig. 2*; [13]: g = 2.0045, $a(1H_\alpha) = 19.30$ G, $a(6H_\varepsilon) = 0.18$ G at 190 K) was the only observable radical species.

Similarly, the open-chain di(*tert*-butyl)malonyl radical was generated by photolysis of 0.018M dibenzoyl peroxide (*Aldrich*) in 1,1,2-trichloro-1,2,2-trifluoroethane (*sds*, > 99.5%) containing 0.89M di(*tert*-butyl) malonate (*Fluka*, > 98%). During photolysis, steady-state ESR spectra revealed the formation of di(*tert*-butyl)malonyl (g = 2.0038, $a(1H_\alpha) = 20.33$ G at 298 K; [14]: g = 2.0039, $a(1H_\alpha) = 20.40$ G at 190 K), but a second radical was also present. This was identified as the 2,2,8,8-tetramethyl-4,6-dioxo-3,7-dioxanonyl radical ($\dot{C}H_2C(CH_3)_2O_2CCH_2CO_2C(CH_3)_3$) (g = 2.0024, $a(2H_\alpha) = 22.16$ G; $a(6H_\gamma) = 1.12$ G at 298 K) and is produced by H-abstraction from the *t*-Bu group of the di(*tert*-butyl) malonate. Its steady-state concentration is seven times smaller than the concentration of di(*tert*-butyl)malonyl, and, therefore, it is ne-

glected in the kinetic analyses. The fully halogenated solvent had to be used, because in other solvents the kinetics of the open-chain malonyl radical indicated considerable side-reactions.

Fig. 1,a, shows a kinetic trace obtained under intermittent photolysis for the cyclic malonyl species at 298 K in an alkene-free solution. The decay is by second-order kinetics ($\tau_2 \approx 780$ µs) slightly perturbed by a first- or pseudo-first-order process ($\tau_{10} = 32 \pm 5$ ms) which we attribute to reactions with the solvent and/or the starting compounds. In the halogenated solvent, the di(*tert*-butyl)malonyl radical also decays by an only slightly perturbed second-order kinetics ($\tau_2 \approx 2000$ µs, $\tau_{10} = 60 \pm 10$ ms), and its relatively long second-order lifetime is due to the rather low steady-state concentrations caused by the low solubility of dibenzoyl peroxide. This also precluded large variations of the alkene concentrations, because the fit equation works well in the limit of $\tau_2/\tau_1 \leq 0.2$ [15] only. Consequently, the majority of experiments on addition reactions was carried out with the cyclic malonyl radical.
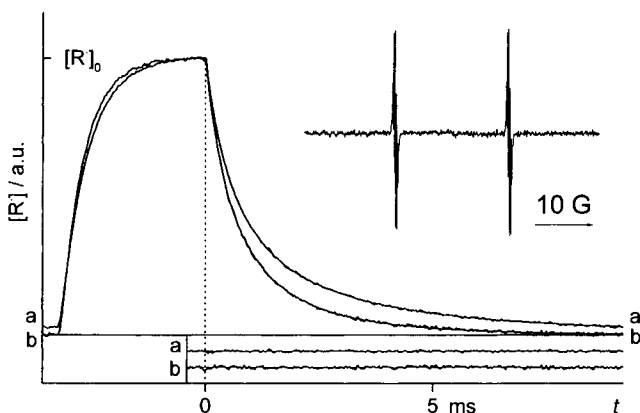

Fig. 1. *Malonyl concentration vs. time* a) *in the absence of alkenes with pure second-order kinetics and* b) *in the presence of 1.2* mm *(trimethyl)(vinyl)silane with a mixed first- and second-order kinetics.* Bottom traces are residuals of fits. The inset shows an ESR spectrum of the 2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl radical.

Using standard procedures and a calibration with $2k_t = 3.3 \cdot 10^9 \mathrm{M}^{-1}\mathrm{s}^{-1}$ for the *t*-Bu self-termination in tetradecane at 300 K [16], the rate constants for the malonyl self-terminations (*Eqn. 4*)

$$2\dot{R} \xrightarrow{2k_t} \text{termination products} \qquad (4)$$

were obtained as $2k_t(300 \text{ K}) = (3.2 \pm 0.2) \cdot 10^9 \text{ M}^{-1}\text{s}^{-1}$ for the cyclic and $2k_t(297 \text{ K}) = (3.1 \pm 0.5) \cdot 10^9 \text{ M}^{-1}\text{s}^{-1}$ for the open-chain radical. These agree fairly well with with $2k_t(298 \text{ K}) = 6.4 \cdot 10^9 \text{ M}^{-1}\text{s}^{-1}$ for $\dot{C}\text{H}(\text{CO}_2\text{H})_2$ in aqueous solution [10]. For the cyclic malonyl radical, the temperature dependence of the termination constant is described by $\log (A/\mathrm{M}^{-1}\mathrm{s}^{-1}) = 11.1 \pm 0.2$ and $E_a = (9.2 \pm 0.6)$ kJ/mol, and is as expected for a diffusion-controlled process [16].

Steady-state ESR spectra taken during continuous photolysis of alkene-containing solutions show the formation of adduct radicals. Their structures reveal addition at the unsubstituted C-atom only, and *Table 1* gives the ESR parameters of the adducts of the cyclic malonyl radical which were identified in this work.

Table 1. *g Factors* (± 0.0001) *and Coupling Constants* ($\pm 0.05G$) *of Adduct Radicals* $RCH_2\dot{C}XY$ (R = 2,2-Dimethyl-4,5-dioxo-1,3-dioxan-5-yl) *from Alkenes* ($CH_2 = CXY$) *in* ($\pm$)*-Propylene Oxide at or close to 298 K*

X	Y	g	H_α	$3H_\beta$	$2H_\beta$	H_γ	Others
H	Me_3C	2.0025	21.26	–	27.56	>0.05	$9H_\gamma$: 0.60
H	Me_3Si	2.0027	20.13	–	23.89	–	$9H_\gamma$: 0.36
H	AcO	2.0029	19.06	–	21.48	0.39	$3H_\delta$: 1.29
H	CHO	2.0046	18.27	–	18.27	–	$1H_\beta$: 1.28
Me	CN	2.0029	–	20.91	20.91	0.25	^{14}N: 3.34
Me	MeO	2.0033	–	20.57	6.94	–	$3H_\gamma$: 2.18
Me	Cl	2.0050	–	22.57	19.16	–	$2^{35}Cl$: 2.09
Cl	Cl	2.0074	–	–	19.91	–	$2^{35}Cl$: 3.90

The rate constants for the addition of the malonyl radicals were determined as usual [3][4] from the pseudo-first-order lifetimes, τ_1, measured for different alkene concentrations. *Fig. 1,b*, shows a kinetic trace for 1.2 mM (trimethyl)(vinyl)silane and a fit which lead to $\tau_1 = 3.09$ ms and $\tau_2 = 8.66$ µs. For each alkene, the pseudo-first-order lifetimes were measured for several alkene concentrations [A]. Plots of τ_1^{-1} *vs.* the concentrations were linear which ensures the validity of the method and yields the addition rate constants k_a from the slopes. *Fig. 2* shows two examples. The non-zero value of τ_1^{-1} for [A] = 0 represents side reactions. Experiments at different temperatures gave the activation parameters for the additions by fits of the *Arrhenius* expression to the data (*Fig. 3*). All results obtained for the cyclic 2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl radical are presented in *Table 2* and for di(*tert*-butyl)malonyl in *Table 3* where the alkenes are ordered according to increasing reactivity of the cyclic species. We also give the applied alkene concentrations and the number of kinetic experiments evaluated for the determination of the activation parameters. The addition to ethene could not be measured, because this alkene was not sufficiently soluble in our solvents.

3. Analysis and Discussion. – The ESR parameters of the adduct radicals (*Table 1*) agree well with those known from the abundant literature for the same or similar species
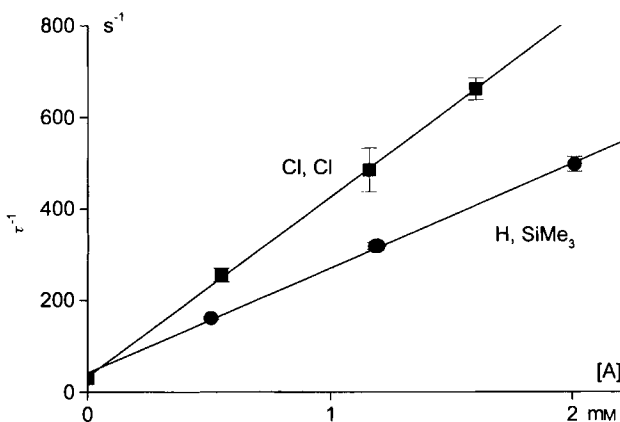

Fig. 2. *Pseudo-first-order plot for the addition of the 2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl radical to 1,1-dichloroethene and to (trimethyl)(vinyl)silane at 298 K*
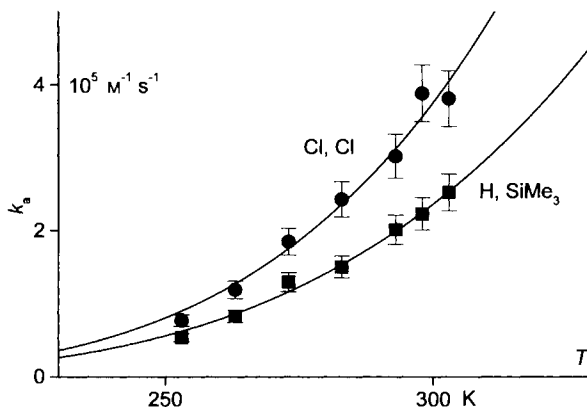
Fig. 3. *Rate constants for the addition of the 2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl radical to 1,1-dichloroethene and to (trimethyl)(vinyl)silane at various temperatures and fits to the* Arrhenius *law*

Table 2. *Absolute Rate Constants[a]) at 298 ± 1 K, Frequency Factors A[a]), and Activation Energies E$_a$[a]) (temperature Range 253–303 K) for the Addition of the 2,2-Dimethyl-4,5-dioxo-1,3-dioxan-5-yl Radical to Alkenes* ($CH_2 = CXY$) *in (±)-Propylene Oxide*

X	Y	c[mM]	n	$k_{298}[10^5 \text{ M}^{-1}\text{s}^{-1}]$	E$_a$ [kJ/mol]	$\log(A/\text{M}^{-1}\text{s}^{-1})$
H	Cl	1.00–5.02	40	1.06 (1)	21.0[b]	
H	CHO	1.02–4.63	87	1.10 (2)	19.7 (7)	8.5 (+ 1/ − 1)
H	CO$_2$Me	1.69–6.28	91	1.12 (3)	21.2 (15)	8.7 (+ 2/ − 4)
H	CN	1.10–2.98	107	1.49 (4)	21.7 (11)	8.9 (+ 2/ − 3)
H	Me	2.20–4.31	18	1.67 (7)	19.8[b]	
H	Me$_3$C	0.89–2.18	137	1.92 (3)	18.6 (6)	8.6 (+ 1/ − 1)
H	Et	1.14–3.35	37	2.22 (3)	19.1[b]	
H	Me$_3$Si	0.51–2.16	87	2.23 (1)	17.9 (10)	8.5 (+ 1/ − 2)
H	EtO	0.54–1.12	58	3.02 (12)	17.7 (14)	8.6 (+ 2/ − 4)
Me	Me	0.27–0.53	24	3.79 (14)	17.8[b]	
Cl	Cl	0.55–1.60	58	3.88 (11)	19.2 (16)	8.9 (+ 2/ − 5)
H	AcO	0.24–0.70	60	3.95 (20)	18.8 (15)	8.8 (+ 2/ − 4)
Me	MeO	0.24–0.86	63	4.00 (20)	17.1 (8)	8.6 (+ 1/ − 2)
Me	AcO	0.25–1.47	72	5.84 (20)	16.8 (13)	8.7 (+ 2/ − 3)
Me	CN	0.24–1.69	75	6.00 (14)	17.0 (6)	8.7 (+ 1/ − 1)
Me	Cl	0.19–0.77	77	9.20 (17)	16.4 (14)	8.8 (+ 2/ − 4)
Me	CO$_2$Me	0.23–0.96	67	10.6 (4)	14.8 (11)	8.9 (+ 1/ − 1)
H	Ph	0.12–0.42	38	11.5 (5)	15.5 (10)	8.8 (+ 1/ − 2)
Me	Ph	0.10–0.51	45	13.3 (4)	15.0 (7)	8.7 (+ 1/ − 2)
Ph	Ph	0.05–0.16	36	24.0 (20)	12.9 (5)	8.6 (+ 1/ − 1)

[a]) Standard deviations in units of the last digit given in brackets.   [b]) Estimated with $\log(A/\text{M}^{-1}\text{s}^{-1}) = 8.7$

[17] and deserve no further comment, except that, for several cases, a γ-coupling to a single proton was found which reensures the addition of malonyl to the unsubstituted alkene C-atom.

As evident from *Tables 2* and *3*, the rate constants of the two malonyl species are rather similar and deviate from each other for all alkenes by less than a factor of two. A comparison with the other radicals of our series [3][4] shows that both are rather

Table 3. *Absolute Rate Constants[a]) at 298 ± 1 K, Frequency Factors* A[a]), *and Activation Energies* E$_a$[a]) *(temperature Range 253–310 K) for the Addition of the Di(tert-butyl)malonyl Radical to Alkenes* ($CH_2 = CXY$) *in Frigen 113*

X	Y	c [mM]	n	$k_{298}[10^5\ M^{-1}s^{-1}]$	E$_a$ [kJ/mol]	$\log(A/M^{-1}s^{-1})$
H	CHO	1.52–2.53	29	2.10 (11)	17.2 (8)	8.4 (+ 1/– 2)
H	CO$_2$Me	1.80–3.60	21	1.19 (2)	17.7 (16)	8.2 (+ 2/– 5)
H	CN	1.11–4.96	43	1.37 (2)	19.0 (8)	8.5 (+ 1/– 2)
H	Me$_3$C	2.43–4.14	24	1.08 (2)	18.1 (8)	8.2 (+ 1/– 2)
H	Me$_3$Si	1.11–2.65	56	1.30 (4)	17.9 (89	8.2 (+ 1/– 2)
Me	MeO	0.82–1.63	41	2.60 (19)	16.2 (10)	8.2 (+ 2/– 2)

[a]) Standard deviations in units of the last digit given in brackets.

unselective, since the rate constants vary with alkene substitution only by a factor of 24. The overall reactivity of the malonyl radicals is very high and even higher than that of the methyl radical [3i].

There are only a few rate constants with which our data can be compared. *Giese et al.* [7] reported relative addition rate constants for dimethyl and diethylmalonyl radicals and α- and ring-substituted styrenes. In agreement with our findings, they observed a low selectivity. In particular, they found k_{383} [1,1-diphenylethene]/k_{383}[α-methylstyrene] = 0.95 and 1.2 in toluene at 383 K, whereas we obtained a ratio of 1.8 at 298 K, *i.e.*, a fairly similar value. *Citterio et al.* [9] measured relative rate constants for the addition of the diethyl-α-benzylmalonyl radical to a variety of alkenes and alkynes at 333 K in toluene. Assuming an absolute rate constant of $8 \cdot 10^6\ M^{-1}s^{-1}$ for styrene, they arrived at addition rate constants which are by factors of 2 to 6 lower than our data, but their value for styrene is too high. Finally, *Diart* and *Roberts* [8] used an indirect ESR technique to determine addition constants for diethylmalonyl and alkenes at 221 K in cyclopropane. With a rather high malonyl self-termination constant of $10^{10}\ M^{-1}s^{-1}$, they obtained $7.3 \cdot 10^3\ M^{-1}s^{-1}$ for ethene, $1.4 \cdot 10^5\ M^{-1}s^{-1}$ for propene, and $5.9 \cdot 10^6\ M^{-1}s^{-1}$ for 2-methylprop-1-ene. In view of our data, the first value seems somewhat low now and the others are high. From the parameters given in *Table 2*, we calculated a reactivity ratio for the addition of the cyclic malonyl to 2-methylprop-1-ene and propene of *ca.* 3 whereas *Diart* and *Roberts* found *ca.* 42 for their open-chain species. All previous authors attributed an electrophilic character to malonyl radicals, since they react less readily with electron-deficient than with electron-rich alkenes and alkynes. This is also seen in *Tables 2* and *3* and will be quantified below.

In the discussion, we first consider the frequency factors. For the addition of the cyclic malonyl to the mono- and 1,1-disubstituted alkenes, they are all in the narrow range of $8.5 < \log(A/M^{-1}s^{-1}) < 8.9$ and show no specific variation with the alkene substituents. Therefore, the spread is presumably caused by an error compensation of the *Arrhenius* parameters. The average is $\log(A/M^{-1}s^{-1}) = 8.7 \pm 0.1$, and, with this value, four missing activation energies in *Table 2* were calculated from the rate constants. The open-chain di(*tert*-butyl)malonyl radical has an average frequency factor of $\log(A/M^{-1}s^{-1}) = 8.2 \pm 0.2$, which is definitively lower than that of the cyclic species. Previously, we found an average frequency factor for the addition of primary radicals to alkenes $\log(A/M^{-1}s^{-1}) = 8.5 \pm 0.3$ [3, 4] (cyanomethyl: 8.7 ± 0.3, (*tert*-butoxy)carbonylmethyl:

8.4 $\pm$ 0.1, hydroxymethyl: 8.1 $\pm$ 0.1, benzyl: 8.9 $\pm$ 1.0, and methyl: 8.6 $\pm$ 0.5), and for tertiary radicals a lower average of $\log(A/\text{M}^{-1}\text{s}^{-1}) = 7.2 \pm 0.8$ (*tert*-butyl: 7.3 $\pm$ 0.4, 2-hydroxyprop-2-yl: 6.4 $\pm$ 1.0, and 2-cyanoprop-1-yl: 7.7 $\pm$ 1.0). The order-of-magnitude similarity of all the frequency factors indicates rather similar transition-state structures, as they are also known from theoretical work [18]: While the newly forming bond is still long (210–240 pm), the angle of attack is already tightly prescribed, and there is a considerable out-of-plane deformation at the two newly bonded C-atoms.

Moreover, the clear variation of the frequency factors with radical structure, which emerges from our data, is also very reasonable. Tertiary radicals should loose more motional freedom of the substituents than primary radicals on approach to the transition state, and hence a more negative activation entropy and a higher frequency factor should result. Also as expected, the open-chain secondary malonyl radical has a frequency factor which lies between those of the primary and tertiary radicals. Further, the relatively large frequency factor of the cyclic malonyl is also easily explained. This radical has a rather rigid structure and can not loose much motional freedom in the transition state.

The narrow ranges of the frequency factors for the malonyl additions mean that the variation of the rate constants with the alkene substitution are due to the variation of the activation energy as it was found previously for other C-centered radicals [3][4]. To rationalize the substituents effects we will now seek correlations of the activation energies with the reaction enthalpies and, for polar effects, with alkene ionization potentials and electron affinities. Steric effects are not considered since they should be small for additions at the unsubstituted C-atom, and since an inspection of our data does not reveal clear trends. The separation of the enthalpic and the polar effects will be difficult, because the malonyl radicals are rather unselective, and the variations of the activation energies are small. However, *Tables 2* and *3* reveal that the activation energies of the open-chain radical are nearly all significantly lower that those of the cyclic species, and the average difference of *ca.* 1.7 kJ/mol between the activation energies of the two radicals should also be explained.

To quantify the enthalpy effect, we estimate the reaction enthalpy H_r of the addition step as before [3][4] by considering the reaction sequence

$$\text{R–H} + \text{CH}_2 = \text{CXY} \rightarrow \dot{\text{R}} + \dot{\text{H}} + \text{CH}_2 = \text{CXY} \rightarrow \dot{\text{H}} + \text{RCH}_2\dot{\text{C}}\text{XY} \rightarrow \text{RCH}_2\text{CHXY} \quad (5)$$

from which it can be expressed in terms of heats of formation H_f of stable compounds and bond dissociation energies *BDE* via

$$H_r(\dot{\text{R}}) = H_f(\text{RAH}) - H_f(\text{RH}) - H_f(\text{A}) + BDE(\text{RA–H}) - BDE(\text{R–H}) \quad (6)$$

where A stands for the alkene. Since $H_f(\text{RAH})$ and $BDE(\text{RA–H})$ are known for many compounds with R = CH_3 but not for R = malonyl, we use here the values of H_r [3i] for methyl-radical additions to the same 20 alkenes and then increment for the substitution via

$$H_r(\dot{\text{R}}) = H_r(\dot{\text{C}}\text{H}_3) + H_f(\text{RAH}) - H_f(\text{CH}_3\text{AH}) - H_f(\text{RH})$$
$$+ H_f(\text{CH}_4) - BDE(\text{R–H}) + BDE(\text{CH}_3\text{–H}) \quad (7)$$

assuming that $BDE(\text{RA–H})$ is not influenced by the change of the radical R. The heats of formation $H_f(\text{RH})$ of the malonic-acid derivatives and of the products $H_f(\text{RAH})$ seem unknown. Hence, we determined the heats of combustion H_c for RH and R–C_2H_5 with

R = *Meldrum*'s acid and dimethylmalonyl (substances from *Aldrich* (98%); the ethylated *Meldrum*'s acid was synthesized as described in [19]) with a bomb calorimeter (model *Rekord, Julius Peters KG*). This yielded H_f for the compounds and allowed the estimation of H_r for the additions of the cyclic malonyl and of the di(*tert*-butyl)malonyl to ethene with the additional adoption of $BDE(R-H) = 387$ kJ/mol for the cyclic and $BDE(R-H) = 398$ kJ/mol for the open-chain species [20]. The results obtained using *Eqn. 7* are given in *Table 4* and render the addition of the cyclic malonyl to ethene by $\Delta H_r = (42 \pm 29)$ kJ/mol and of the open-chain radical by (22 ± 16) kJ/mol less exothermic than the addition of $\dot{C}H_3$. Obviously, the cyclic radical is considerably more stabilized than the open-chain species. Secondly, we calculated $H_f(RH)$ and $H_f(RAH)$ for the 20 cases of addition by increments [21] and then estimated the reaction enthalpies by *Eqn. 6* with $H_f(A)$ and $BDE(A-H)$ from [3i]. This led to an average value for the differences H_r (malonyl) $- H_r(\dot{C}H_3)$ of 41.7 kJ/mol for the cyclic and 28.6 kJ/mol for the open-chain radical which agree with the calorimetric results. As final differences to methyl, the experimental values of 42 and 22 kJ/mol were adopted.

Table 4. *Heats of Combustion (H_c)[a], Estimated Heats of Formation (H_f)[a]) for $R-X$ (R = 2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-yl (R^1) and Dimethylmalonyl (R^2)), Reaction Enthalpies (H_r)[a] for the Addition of Malonyl Radicals R to Alkenes, and Differences of the Reaction Enthalpies (ΔH_r)[a] at 295 ± 2 K*

R	X	$H_c(R-X)$ [kJ/mol]	$H_f(R-X)$ [kJ/mol][b]	$H_r(R)$ [kJ/mol][c]	ΔH_r [kJ/mol][d]
R^1	H	− 2664 (6)	− 840 (6)		
R^1	CH_3	− 3314 (4)	− 869 (4)		
R^1	C_2H_5	− 3983 (12)	− 880 (12)	− 57 (25)	42 (29)
R^2	H	− 2309 (4)	− 802 (4)		
R^2	C_2H_5	− 3618 (3)	− 851 (3)	− 77 (12)	22 (16)

[a]) Standard deviation in units of the last digit given in brackets. [b]) $H_f(R-X) = x \cdot H_f(CO_2) + y \cdot H_f(H_2O) - H_c(C_xH_yO_4)$ with $H_f(CO_2) = 393.51$ kJ/mol, $H_f(H_2O) = 285.83$ kJ/mol [23][25]. [c]) Calculated with *Eqn. 7*. [d]) $\Delta H_r = H_r$(malonyl) $- H_r(\dot{C}H_3)$; $H_r(\dot{C}H_3)$ from [3i].

Fig. 4 shows the activation energies for both radicals plotted against the reaction enthalpies H_r. The linear regression is

$$E_a \text{ [kJ/mol]} = (20.8 \pm 1.5) + (0.038 \pm 0.018) \cdot H_r \text{ [kJ/mol]} \qquad (8)$$
$$r = 0.39, \text{ 26 data}$$

The correlation is rather poor, and its slope is lower than for other radicals (+ 0.2 [3][4n]). Nevertheless, the dependence on the reaction enthalpy is significant and can explain the systematically lower activation energies of the open-chain malonyl radical. Yet, the reaction enthalpy cannot be the only important factor, since the malonyl radicals react faster than methyl though they are considerably stabilized. Hence, their reactions must be accelerated by polar effects.

These polar effects are usually discussed in terms of the state correlation diagram [3i][22] which considers the transition state as a combination of four principal bonding configurations of the parent reaction system $\dot{R}$ + A, namely $\dot{R}A$, $\dot{R}^3A$, R^+A^-, and $R^-\dot{A}^+$. Here $\dot{R}A$ represents the educt ground-state configuration, for $\dot{R}^3A$ the alkene is excited to the lowest triplet state, and R^+A^- and $R^-\dot{A}^+$ are the energetically lowest
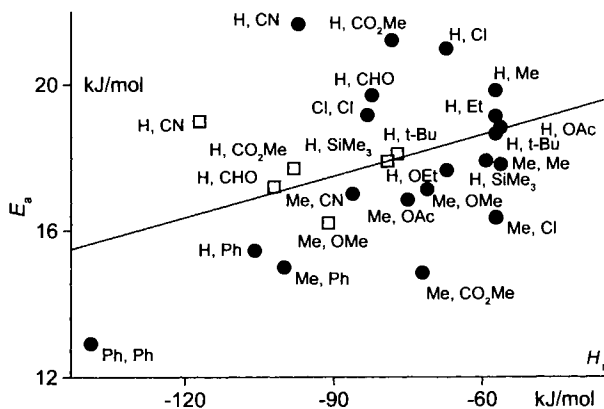
Fig. 4. *Activation energies for the addition of malonyl radicals to alkenes* vs. *estimated reaction enthalpies.* Closed symbols: cyclic, open symbols: open-chain malonyl

charge-transfer states. For the separated reactants, the energies of the two polar states are given by $IP(\dot{R}) - EA(A)$ and $IP(A) - EA(\dot{R})$, respectively, where IP and EA are the ionization potentials and electron affinities of radicals and alkenes, respectively. These high-lying states are lowered considerably on approach to the transition state by the *Coulomb* interaction, and then mix with the two unpolar states. This decreases the reaction barrier. In the frontier molecular-orbital model, this is expressed by stabilizing SOMO-LUMO and SOMO-HOMO interactions in the transition state. IP and EA of the alkenes are known [23]; however, for the malonyl radicals only estimates are available. Thus, for an open-chain malonyl $IP(\dot{R}) = 11$ eV has been suggested [9], and the electron affinity $EA(\dot{R})$ should be larger than 1.8 eV, the value for a monocarboxy-substituted methyl radical [24]. These values are used here for both radicals which is certainly only a rough approximation.

The high ionization potential of malonyl radicals makes a nucleophilic behavior very unlikely, and, in fact, plots of E_a vs. EA of the alkenes show no significant correlation. *Fig. 5* shows the activation energies plotted vs. the alkene ionization potentials. The correlation is rather reasonable with

$$E_a \text{ [kJ/mol]} = (-0.2 \pm 3.9) + (1.89 \pm 0.41) \cdot IP \text{ [eV]} \qquad (10)$$
$$r = 0.69, \text{ 26 data}$$

Hence, malonyl radicals do express an electrophilic character, and the favorable charge transfer in the transition state increases the addition rate constants even beyond those of methyl. The electrophilicity is also clearly shown by the fact that for all cases in *Table 3* α-methylated alkenes react considerably faster than unmethylated ones which is consistent with the increased electron density of the double bond. However, malonyl radicals are much less electrophilic than perfluoro-substituted alkyl species, as is seen in the following data from this work and [5].

$$\text{cyclic malonyl} \quad \log(k_{298}/\text{M}^{-1}\text{s}^{-1}) = 9.0 - 0.36 \cdot IP \text{ [eV]} \qquad (11)$$
$$\dot{C}F_3 \quad \log(k_{298}/\text{M}^{-1}\text{s}^{-1}) = 12.0 - 0.49 \cdot IP \text{ [eV]} \qquad (12)$$
$$C_2F_5\dot{C}F_2 \quad \log(k_{298}/\text{M}^{-1}\text{s}^{-1}) = 12.5 - 0.56 \cdot IP \text{ [eV]} \qquad (13)$$
$$(CF_3)_3\dot{C} \quad \log(k_{298}/\text{M}^{-1}\text{s}^{-1}) = 21.0 - 1.49 \cdot IP \text{ [eV]} \qquad (14)$$
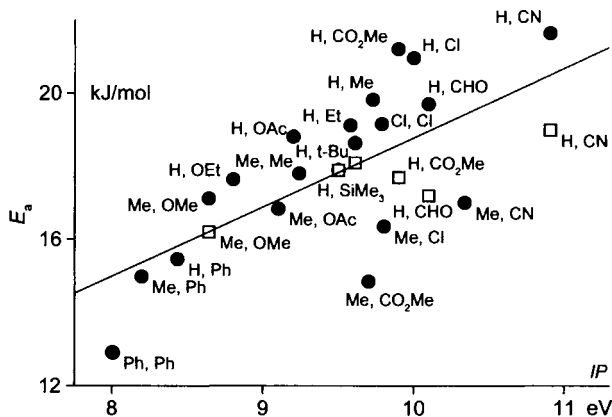
Fig. 5. *Activation energies for the addition of malonyl radicals to alkenes* vs. *alkene ionization potentials.* Closed symbols: cyclic, open symbols: open-chain malonyl.

As expected for electrophilic radicals, the increase of the slopes in the series reflects the increase of the electron affinities of the radicals with EA(malonyl) ≥ 1.8 eV, $EA(\dot{C}F_3) = 2.3$ eV, $EA(C_2F_5\dot{C}F_2) = 2.6$ eV, and $EA((CF_3)_3\dot{C}) = 3.4$ eV [25]. The electrophilicity of these radicals is reflected by the high electron affinities, as nucleophilic radicals have particularly low ionization potentials.

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