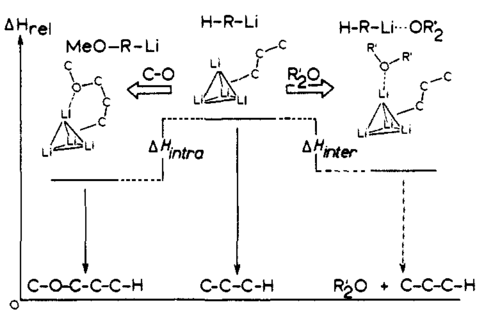

Figure 1. Relative enthalpies of formation (per mole of RLi) of tetrameric alkyllithiums and (γ-alkoxy)alkyllithiums, as determined from differences between heats of protonation (represented by solid vertical arrows). For clarity, only one (γ-alkoxy)alkyl group and one ether molecule (R'_2O) are shown.

Table I. Enthalpies of Protonation ($\Delta H_{r,ZH}$; Z = *s*-BuO, Br; kJ/mol of RLi, 25 °C) of Saturated Organolithium Compounds[a]

RLi	deg of assocn[b]	$\Delta H_{r,s\text{-BuOH}}$[b]	$\Delta H_{r,BrH}$[c]	$\Delta H_{r,BrH} - \Delta H_{r,s\text{-BuOH}}$
I	4[d]	−199 + 4		
II	4[e]	−190 ± 2		
III	4[e]	−199 ± 2	−333 ± 6[f]	−134
IV	4?[g]	−190 ± 3		
IX	4[h]	−240 ± 5	−374 ± 4[i]	−134
X	6[e]	−219 ± 2		
XI	6[j]	−221 ± 4	−354 ± 4[i]	−133
XII	4[e]	−222 + 5	−360 ± 9[f]	−138

[a] All operations were carried out in evacuated sealed vessels using the break seal technique. In the solutions of RLi no impurities were detectable by NMR and double titration. [b] In benzene. [c] In pentane. [d] Reference 6. [e] This work; determined by the method of ref 16. [f] Reference 8b. [g] Insufficiently soluble for measurement, presumably tetrameric. [h] Reference 17. [i] Reference 15. [j] Cf. reference 2b.

s-BuLi (IX), *n*-PrLi (X), *n*-BuLi (XI), and 2-norbornyllithium (exo:endo ca. 1, XII), respectively, with a slight excess of *s*-BuOH (0.2 M in benzene) were measured[14] and are given in Table I together with some earlier values [$\Delta H_{r,BrH}$(25 °C)] obtained with gaseous HBr in pentane.[8b,15]

The very similar values of $\Delta H_{r,BrH} - \Delta H_{r,s\text{-BuOH}}$ attest to the internal consistency of the two sets of data. If the same *relative enthalpy of formation in benzene* is assigned to protonation products differing only by the presence or absence of OMe at C-γ the difference between two values of ΔH_r must be ascribed to the *difference between the relative enthalpies of formation in benzene per mole of RLi* of the two lithium compounds compared. Lowerings of relative enthalpies of formation (enthalpies of intramolecular etheration, ΔH_{intra}) incurred by transformation of a "normal" organolithium compound (H–R–Li) into its γ-methoxy analogue (MeO–R–Li) are (see Table I, kJ/mol of RLi; Figure 1) −41 (IX → I), −23 (XII → III), and −30 [av X → II (or IV) and XI → II (or IV)]. The value of $|\Delta H_{intra}|$ is largest in the *s*-butyl system in which both H–R–Li (IX) and MeO–R–Li (I) have the same degree of aggregation. It is slightly larger than that of the "initial enthalpy of interaction" (ΔH_{inter} = −36 kJ/mol of THF) obtained for the sterically more demanding *intermolecular* formation of *i*-Pr_4Li_4·THF in benzene (mole ratio THF_{added}:*i*-PrLi = 0.08).[3] The smaller value of $|\Delta H_{intra}|$ found for the 2-norbornyl system shows that on an (*exo*-2-norbornyl)$_4Li_4$ cluster even intramolecular etheration by γ-MeO is weakened by steric crowding. For primary alkyllithiums where H–R–Li (X, XI) occurs predominantly as a hexamer and MeO–R–Li (II, IV) as a tetramer the γ-OMe-induced lowering of the relative enthalpy of formation per mole of RLi is smaller than for the *s*-alkyllithiums since it is the sum of opposing contributions by the enthalpy of deaggregation ($\Delta H_{6\to4}$) and ΔH_{intra} of an *n*-alkyllithium tetramer (eq 1).

$$\Delta H_{6\to4} + \Delta H_{intra} = -30 \text{ kJ/mol of RLi} \qquad (1)$$

Assuming that for the sterically less encumbered primary alkyllithiums ΔH_{intra} matches ΔH_{inter} more closely than found for I and *i*-PrLi, eq 1, with ΔH_{inter} instead of ΔH_{intra}, may be substituted into eq 3, which specifies the enthalpy changes constituting the enthalpy of etheration of *n*-BuLi by THF in benzene (eq 2).[4]

$$n\text{-}Bu_6Li_6 + 1.5p\text{THF} \rightleftharpoons 1.5n\text{-}Bu_4Li_4\cdot p\text{THF}$$
$$\Delta H(\text{benzene, 30 °C}) = -120 \text{ kJ/mol of } n\text{-}Bu_6Li_6 \qquad (2)$$

$$-120 = 6\Delta H_{6\to4} + 1.5p\Delta H_{inter} \qquad (3)$$

$$p = \frac{60}{-45 - 1.5\Delta H_{6\to4}} + 4 \qquad (4)$$

The resulting relationship (eq 4) gives the number (p) of THF molecules bonded to one molecule of *n*-Bu_4Li_4 in benzene as a function of $\Delta H_{6\to4}$. Choosing values of $\Delta H_{6\to4}$ between 10 and 25 kJ/mol of RLi[18] [ΔH_{inter} (=ΔH_{intra}) = −40 to −55 kJ/mol of RLi] one obtains values of p ranging from 3.0 to 3.3 in agreement with the finding that the average number of THF molecules that can maximally be bonded to *n*-Bu_4Li_4 in cyclohexane is 3.6, while "the equilibria appear to proceed to a smaller extent in benzene".[2b,19]

Acknowledgment. We are grateful to Prof. Dr. F. Bickelhaupt, Dr. O. S. Akkerman, and G. Schat for making available the calorimeter developed by them and providing advice and practical help in its use.

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(13) Thermochemistry also suggests the absence of tetramers whose CH_2CH_2Y moieties are in the open-chain form. Their enthalpies of intramolecular Li···Y coordination would not differ greatly from ΔH_{intra} (vide infra). For a $\Delta H_{Li\cdots Y}$ of, say, −35 kJ/mol of RLi presence of 5% of open-chain CH_2CH_2Y requires $\Delta S_{Li\cdots Y}$ to amount to −93 J/(mol of RLi deg). This value seems unrealistic since ΔS^{*} for interchange (supposedly through ring opening–ring closure) of V and VI (Y = OMe, NMe_2) is in the range of 46 J/(mol of RLi deg).[10,11]

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Epoxidations of Olefins by Peroxy Intermediate Generated in Situ from CCl_4 and Superoxide[†]

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Considerable interest has been focused on the reactivities of the peroxy intermediate $Cl_3COO\cdot$,[1] which may be formed in the reaction of superoxide with CCl_4. Sawyer has reported that in aprotic solvents, superoxide (O_2^-) can oxygenate CCl_4 to yield $HOC(O)O^-$ as an overall product via formation of $Cl_3COO\cdot$ radical and Cl_3COO^- anion.[2] The initial step is believed to be some form of interaction between O_2^- and CCl_4. The resulting

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Table I. Cooxidations of Olefins during the Oxidation of CCl_4 with Superoxide[a]

substrate	product [%]	recovery
styrene	styrene oxide [56 (0)],[b] benzaldehyde [9 (0)], benzoic acid [8 (0)]	11 (91)
trans-stilbene	*trans*-stilbene oxide [62 (0)],[c] benzaldehyde, [11 (0)], benzoic acid [11 (0)]	3 (89)
β-methylstyrene	β-methylstyrene oxide [83 (2)], benzaldehyde [7 (0)], benzoic acid [9 (<1)]	0 (93)
α-methylstyrene	α-methylstyrene, oxide [79], acetophenone [19]	0
cis-stilbene	stilbene oxide, [33],[d] benzaldehyde [7], benzoic acid [6]	26
2-cyclohexen-1-one	2,3-epoxycyclohexanone [4 (0)]	80
cyclohexene	1,2-epoxycyclohexane [73], 2-cyclohexen-1-one [9]	nd[e]
1-methylcyclohexene	1,2-epoxy-1-methylcyclohexene [88 (<1)]	nd
phenanthrene	phenanthrene oxide [11]	86
1-octene	1,2-epoxyoctane, [9 (0)], octanoic acid [<1 (0)]	nd

[a] The reaction mixtures contained 0.3 mmol of substrate, 15 mmol of CCl_4, 3 mmol of KO_2, and 0.3 mmol of 18-crown-6 in CH_3CN solution. Reactions were allowed to proceed for 4–24 h at 10 °C. [b] Values in parentheses indicate yields in the absence of CCl_4. [c] No oxide was formed without KO_2. [d] *trans*-Stilbene oxide (31%) + *cis*-stilbene oxide (2%). [e] nd = not determined.

activated complex can then dissociate to give chloride ion, dioxygen, and $\cdot CCl_3$ radical, followed by coupling of the $\cdot CCl_3$ radical and dioxygen to form $Cl_3COO\cdot$ radical. Though there are many reports of O_2^- being very toxic to living cells,[3] the reactivity of superoxide alone is not as vigorous in vitro as those of other active oxygen species, e.g., $\cdot OH$, $^1O_2$.[4] We have found that the acylperoxy radical [$R{-}C(O)OO\cdot$] or the acylperoxy anion [$R{-}C(O)OO^-$], generated in situ by treatment of acyl halide with superoxide, is much more active as an oxidizing agent than superoxide alone.[5] From these results, we can expect the reaction of superoxide with CCl_4 to induce the formation of the active species which causes the biological toxicity. A greater reactivity might be expected because of the electron-withdrawing nature of the trichloromethyl group. This paper reports our finding that superoxide reacts with CCl_4 in aprotic solvents to yield the active peroxy species, which can oxidize olefins to the corresponding epoxides.

In the general procedure, styrene was added to a heterogeneous CH_3CN solution of potassium superoxide and CCl_4 in the presence of 18-crown-6 with stirring at 10 °C. Styrene and its derivatives afforded their correponding epoxides in excellent yields (Table I). As shown in Table I, the oxidations were dependent upon the presence of KO_2 and CCl_4. When *cis*-stilbene was used as substrate, the major product was *trans*-stilbene oxide (yield, 31%), not *cis*-stilbene oxide (yield, 2%). Cyclic olefins were also epoxidized in good yields, while oxidations of the acyclic olefin and the double bond in the α,β-unsaturated ketone were detected in very low yields of 9% (1-octene → 1,2-epoxyoctane) and 4% (2-cyclohexen-1-one → 2,3-epoxycyclohexanone), respectively. Peroxide ion (O_2^{2-}) can not be an actual species, because superoxide will not disproportionate to give O_2^{2-} in aprotic media.[6] The results that these epoxidations are neither nucleophilic nor stereospecific suggest that the peroxy radical intermediate is the responsible agent. Other additives, chloride compounds, were also found to be effective for oxidizing *trans*-stilbene to the epoxide under mild conditions. [yields of *trans*-stilbene oxide: 63% (Cl_3CCCl_3), 53% (F_3CCCl_3), 72% ($BrCCl_3$), 50% ($Cl_2C{=}CCl_2$), 43% ($Cl_2C{=}CHCl$), 42% ($F_3CCBrClH$), 27% ($CHCl_3$), 26% ($PhCCl_3$), 2% (*p,p'*-DDT)]

We examined the time courses of the production of α-methylstyrene oxide and acetophenone in the oxidation of α-methylstyrene. The maximal yield of acetophenone (19%) was obtained within 3 h, while the formation of the epoxide (79%) required longer to achieve the maximal yield. Furthermore, when the oxide was used as substrate, 96% of the starting material was recovered. This revealed that the epoxide is stable in the reaction system and acetophenone is not formed via the epoxide. α-Methylstyrene, which is a more electron-rich olefin than styrene, was more readily oxidized when equimolar amounts of styrene and α-methylstyrene were used as substrates.[7] DABCO, which is known to reduce $Cl_3COO\cdot$ to Cl_3COO^-, can inhibit the oxidation of *trans*-stilbene (Figure 1).[1c] These results offer evidence for the oxidation involving attack not by Cl_3COO^- but by $Cl_3COO\cdot$, which should be formed from the complex of CCl_4 and O_2^-. The initial form [$CCl_4O_2^-$] of interaction between O_2^- and CCl_4 may be followed by dioxygen and $Cl_3C\cdot$ with subsequent coupling of the $Cl_3C\cdot$ radical and O_2 in the solvent cage to form $Cl_3COO\cdot$ as reported by Sawyer et al.[2b] The reaction mechanism concerning the solvent cage can be supported by the data in which the epoxide yields are independent of O_2 concentrations in the reaction mixtures. [Epoxidation yields of *trans*-stilbene: 64% (under 100% O_2), 62% (under air), and 54% (under Ar atmosphere).]

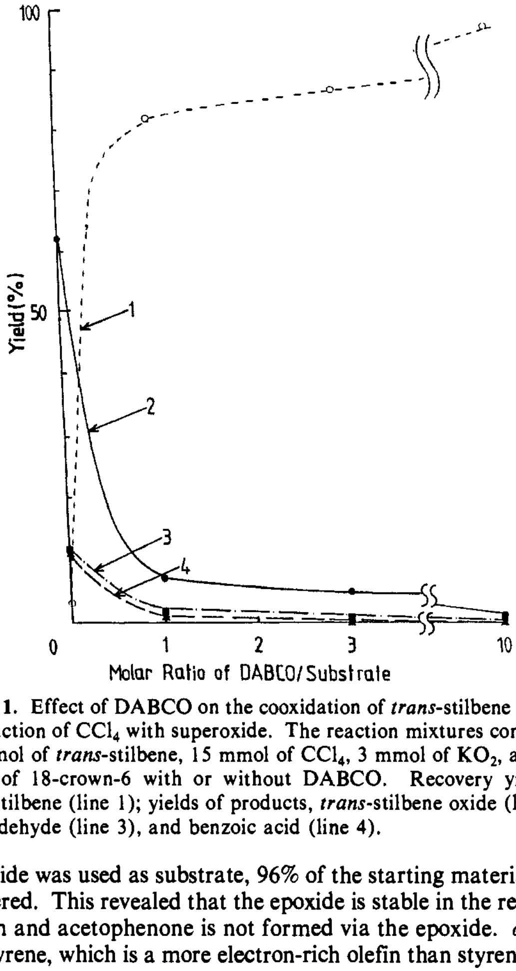

Figure 1. Effect of DABCO on the cooxidation of *trans*-stilbene during the reaction of CCl_4 with superoxide. The reaction mixtures contained 0.3 mmol of *trans*-stilbene, 15 mmol of CCl_4, 3 mmol of KO_2, and 0.3 mmol of 18-crown-6 with or without DABCO. Recovery yield of *trans*-stilbene (line 1); yields of products, *trans*-stilbene oxide (line 2), benzaldehyde (line 3), and benzoic acid (line 4).

The results obtained can be accounted for by the formation of an oxidizing agent such as a peroxy intermediate, though the

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[6] The reaction of *trans*-stilbene with Na_2O_2 in palce of KO_2 in the presence of 18-crown-6 and CCl_4 in CH_3CN afforded not oxidized products but the starting material (91%).

[7] Reaction conditions of 2.5 mmol of α-methylstyrene, 2.5 mmol of styrene, 0.5 mmol of KO_2, and 0.05 mmol of 18-crown-6 yielded 35% α-methylstyrene oxide and 5% styrene oxide.

detailed reaction mechanisms are not clear. The CCl_4–potassium superoxide reaction should yield an active intermediate, the $Cl_3COO\cdot$ radical, which oxidizes electron-rich olefins to afford the corresponding epoxides and which is a markedly more potent oxidizing agent than superoxide alone.

Layered Double Hydroxides as Supported Anionic Reagents. Halide Ion Reactivity in $[Zn_2Cr(OH)_6]X\cdot nH_2O$

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Several new families of heterogeneous catalysts recently have been synthesized by intercalating metal ions and cationic metal complexes between the negatively charged layers of smectite clay minerals.[1,2] A complementary class of layered compounds exist in which the charge on the layers and gallery ions is the reverse of that found for smectite clays. These are the layered double hydroxides (LDH's) of the type $[M_x^{II}M_y^{III}(OH)_{2(x+y)}]A_{y/n}\cdot zH_2O$.[3-5] The positively charged layers are brucitelike ($Mg(OH)_2$) with trivalent cations substituting for divalent cations in octahedral sites of the hydroxide sheet. Typically, the ratio y/x is in the range 0.20–0.50. In naturally occurring LDH minerals the interlayer anion A^{n-} is most commonly carbonate as in hydrotalcite, $Mg_6Al_2(OH)_{16}(CO_3)\cdot 4H_2O$, and pyroaurite, $Mg_6Fe_2(OH)_{16}(CO_3)\cdot 4H_2O$. However, a wide range of derivatives containing various combinations of M^{II}, M^{III}, and A^{n-} ions can be synthesized either by direct crystallization[6-9] from aqueous solution or by anion exchange[10] for A^{n-} in a precrystallized host.

LDH's have been investigated as solid ionic conductors[11] and as catalyst precursors,[12,13] but the properties of the pristine compounds as supported anionic reagents or as catalysts for chemical synthesis have not been addressed. Unlike the galleries of smectites, which can be swelled by multiple layers of solvent to mimic a solution-like environment,[1] the galleries of LDH's accommodate only one or two layers of water and other polar molecules. This limitation in gallery swelling, along with the relatively high layer charge density, means that typical organic reagents are unable to penetrate the intracrystal space occupied by the anions. Here we demonstrate that although the gallery anions in a typical LDH are not accessible for direct intracrystalline reaction, they are readily transferred to external edge surfaces for reaction with substrates adsorbed at those sites.

The reactions investigated were simple halide-exchange processes between the halide ions in $Zn_2Cr(OH)_6X\cdot H_2O$ and alkyl halides in the condensed state (toluene) or in the vapor phase. The chloride form of the LDH was prepared by reaction of aqueous $CrCl_3$ with ZnO according to previously described procedures.[14,15]

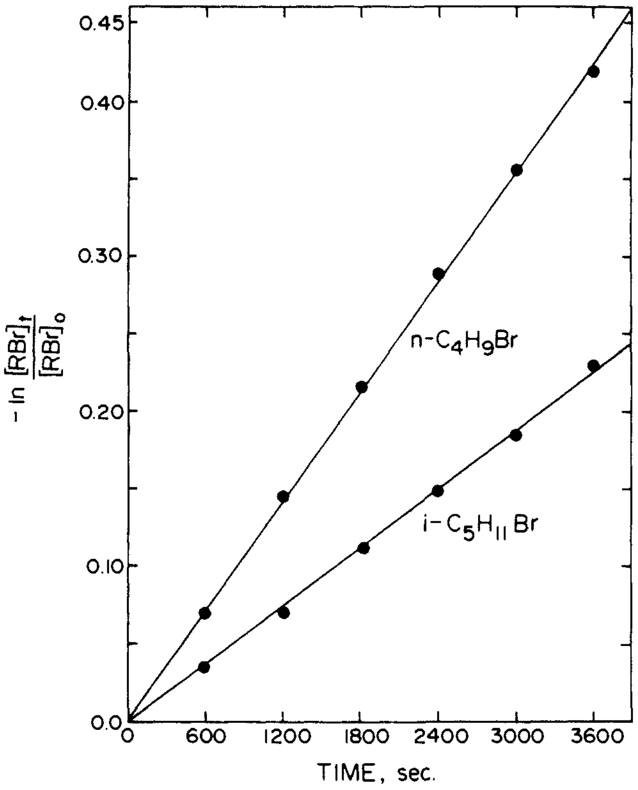

Figure 1. Pseudo-first-order kinetic plots for the reaction of (A) n-butyl bromide and (B) 3-methylbutyl bromide with $Zn_2Cr(OH)_6I\cdot 2H_2O$ in toluene suspension at 90 °C. The LDH was predried at 150 °C under argon prior to reaction. The initial reaction mixtures contained 1.0 mmol of alkyl bromide and LDH in 3.0 mL of toluene. $[RBr]_t/[RBr]_0$ is the fraction of substrate unreacted at time t.

Table I. Pseudo-First-Order Rate Constants[a] (90 °C) for Halide Exchange between Alkyl Bromides in Toluene and $Zn_2Cr(OH)_6I\cdot 2H_2O$

	10^5k_{obsd}, s^{-1} m^{-2}	
alkyl bromide	LDH dried at 25 °C	LDH dried at 150 °C
n-C_4H_9Br	1.1	3.0
n-$C_5H_{11}Br$	1.1	3.6
i-$C_5H_{11}Br$	0.60	1.6
n-$C_6H_{13}Br$	0.83	3.1
n-$C_8H_{17}Br$	0.87	2.4

[a] Rate constants have been normalized per unit surface area of LDH.

The product was identified by X-ray diffraction analysis (d_{003} = 7.7 Å). Exchange of the chloride form with excess 1.0 M NaI solutions afforded the iodide form with d_{003} = 8.3 Å.[15] N_2 BET surface areas were 7.7 and 9.4 m^2/g, respectively, for LDH samples dried under Argon at 25 and 150 °C.

Condensed-phase reactions were carried out in culture tubes containing 3.0 mL of toluene and 1.0 mmol each of LDH and alkyl halide. The reaction mixture was stirred vigorously while being maintained at 90 °C in an oil bath, and samples were withdrawn periodically for analysis by gas chromatography. Reactions of alkyl halides in the vapor phase with LDH were carried out in a microreactor in the temperature range 90–150 °C. The reactor was loaded with 1.0 mmol of LDH and 1.0 mmol of alkyl halide was passed through the LDH under a flow of helium to allow for a contact time of 0.19 s. The products were condensed and analyzed by gas chromatography.

As is illustrated in Figure 1 for n-butyl bromide and 3-methylbutyl bromide, halide exchange between alkyl bromides in toluene and intercalated iodide ions in the LDH followed

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