A Theoretical Study of the Catalytic Activity of Group I Metal Salts in the Homogeneous Liquid-Phase Oxidation

Katsutoshi Ohkubo, Hidetoshi Shimada, Yasuhiro Shiotani, and Masahide Okada
Faculty of Engineering, Kumamoto University, Kurokami-machi, Kumamoto

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A theoretical consideration of the catalytic activity of group I metal salts, especially of lithium ones, for the homogeneous liquid-phase oxidation of hydrocarbons was developed by extended Hückel molecular orbital calculations, with particular reference to the interaction between the salts and molecular oxygen. We made several findings. First, a marked activity of lithium salt-catalysts was reflected by a remarkable "electron-partial occupation" of the lithium cation in their salts. Second, a strong interaction of the lithium catalyst with O_2 occurred at the angle of 15° to the direction of the $1\pi_g$-orbital expansions of O_2. Third, the lithium catalyst participated strongly in the activation of O_2 at the distance of 2 Å—3 Å, increasing the electron-population of one oxygen atom located farther from the lithium cation. Finally, the contribution of the "activated" oxygen molecule to the initiation of the oxidation of hydrocarbons was discussed.

In the field of liquid-phase catalytic oxidations, it is usually accepted that oxidation catalysts such as transition metal compounds[1] exhibit catalytic effects on the acceleration of the reaction rate through the so-called "*Haber-Weiss*"mechanism.[2] On the other hand, the different proposals of some other authors[3–5] have been based on the concept that oxidation catalysts might interact with molecular oxygen to form "*activated*" oxygen. This concept is surely plausible considering that the main product (hydroperoxide) accumulated is little decomposed by the catalyst in low-temperature oxidation in spite of the appreciable amounts of oxygen consumed to hydrocarbons. However, the above concept has not been confirmed precisely on the basis of experimental work.

It is hard to deny that hydroperoxides formed in such small amounts (below 2%[6] of the total conversion, as determined from the amount of O_2 absorbed) during the induction period initiate the oxidation reaction as radical initiators through their thermal or catalytic decompositions. In this case, radicals produced secondarily from such a hydroperoxide take part in the decomposition of the hydroperoxide formed successively.

From our previous works concerning the catalytic behavior of such salt-type catalysts as onium compounds[7–9] and metal salts[10] in the homogeneous liquid-phase oxidation, the phenomena of the increasing rates at the initial stage of the reaction could be well explained by the assumption of an interaction between the catalysts and molecular oxygen; furthermore, this assumption was supported more precisely by a spectroscopic study[11] of the above interaction. Recently, the donor-acceptor interaction[12–14] between organic compounds (donor) and molecular oxygen (acceptor) has been studied in detail in connection with the "*contact charge-transfer complex*";[15–17] a theoretical calculation of this complex can be found in Ref. 18. Moreover, a possible interaction of KCl with O_2 has been confirmed by Känzig and Cohen[19] by a study of the ESR spectra, which indicated the presence of the O_2^- anion. It was found in our recent study[10] that alkali metal salts, in particular lithium salts, promote the oxidation reaction remarkably without an incubation period: this suggests the interaction of the salts with molecular oxygen at the initial, short stage of the reaction.

The aim of this study is to clarify the following points: a) the electronic states of metal salts, especially of lithium salts, and their correlations to the catalytic activity of the salt-type catalysts, b) the mode of the intraction of the catalysts with molecular oxygen, and c) the chemical property of the oxygen molecule "*activated*" through the interaction with the above salt-type catalysts. The extended Hückel method proposed by Hoffman[20] was employed to investigate these items.

Methods of Calculation

The calculations by the extended Hückel method were performed at first on group I metal chlorides and

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[1] For instance, W. F. Brill, *Ind. Eng. Chem.*, **52**, 837 (1960); A. Robertson and W. A. Walters, *J. Chem. Soc.*, **1947**, 492; E. R. Muller, *Ind. Eng. Chem.*, **46**, 562 (1954); N. Ohta and S. Marumo, *Kogyo Kagaku Zassi*, **58**, 798 (1955), and the references cited therein.

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[6] It is generally considered that the hydroperoxide formed (mol) corresponds at most to 98% of the total conversion on the basis of the amount of O_2 absorbed (mol).

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several lithium salts: LiCl, NaCl, KCl, RbCl, LiBr, LiI, LiF, Li_2SO_4, Li_2CO_3, LiO_2CH, $LiO_2CC_2H_5$, $LiNO_3$, $(LiO_2C)_2$, Li_3PO_4, and so on. Secondly, the calculations were carried out for the interaction between LiCl and O_2 with the variation in the bond angles of OOLi at 0°, 10°, 15°, 30°, 60°, and 90° at a fixed distance (O_2–LiCl=3.0 Å). Thirdly, the calculations were performed on the interactions between LiCl and O_2 at the distances (O_2–LiCl) of 1.0—5.0 Å at a fixed angle ($\angle$OOLi=15°). For the calculations, the values of the orbital exponents for H, Li, Na, Rb, Be, C, N, O, P, S, and Cl were taken from the data of Clementi[21], while the valence-state ionization potentials used for the diagonal H-matrix elements (H_{ii}) were supplied by Hinze[22,23] and Pople[24]. These parameters are listed in Table 1. For the off-diagonal matrix elements (H_{ij}), the Wolfsberg-Helmholtz approximation[25] was employed:

$$H_{ij} = K(H_{ii}+H_{jj})S_{ij}/2$$

where the value of K is taken to be 1.75[26] and where S_{ij} is the overlap integral between AO's.

In regard to the bond lengths and angles of the metal salts, they are indicated in the proper tables and figures in this paper. For the H_{ij} of the O atom, there exist three different sets of values for cheking the charge of the atom: H_{ii}(eV)=−36.02 (O 2s) and −18.53 (O 2p) (Method I), −32.38 (O 2s) and −15.85 (O 2p) (Method II), and −35.30 (O 2s) and −13.61 (O 2p) (Method III). Finally, the contour maps of the interaction between the partially-occupied s-Li^+ orbital and $1\pi_g$-orbitals of O_2 were portrayed using the effective nuclear charges of the two atoms as derived from Slater's rule.[27]

Table 1. Parameters used for the calculations

Atom	Orbital exponent	Ionization potential (eV)	
		s	p
H	1.0	13.60	
Li	0.6396	5.39	3.54
Na	0.8358	5.14	3.04
K	0.8738	4.34	2.73
Rb	0.9969	4.18	2.60
Be	0.9560	9.92	5.96
C	1.5679	21.01	11.27
N	1.9170	26.92	14.42
O	2.2266	36.07[a]	18.53[a]
		32.38[b]	15.85[b]
		35.30[c]	13.61[c]
P	1.6288	20.20	12.49
S	1.8273	20.08	13.32
Cl	2.0387	24.02	13.39

a) Method I, b) Method II, c) Method III

Results and Discussion

The Correlation between the Catalytic Activity of the Metal Salt and the Atom Population of its Metal Ion. Before discussing the correlation between the catalytic activity of metal salt and the atomic population of its metal cation (M(M^+)), it is necessary to emphasize that the catalytic activity of metal salt is not directly dependent upon the counter anion of the salt, but upon its metal cation, and that it is affected mediately by the difference in the structures of the anions. Moreover, the counter anion of the effective salt-type catalyst is not required to have a radical as metal halide.[28] Among the group I metal salts tested, lithium salts exhibited a striking catalytic activity for the acceleration of the reaction rate, without the decomposition of the hydroperoxide formed at the initial stage of the oxidation. It was considered that such a remarkable activity of lithium salts was related to the small 2s-lithium orbital "partially occupied" by an electron-inflowing from the counter anion. The lowest vacant s-orbital (speaking strictly, a partially occupied one) of Li^+ would thus play an important role in the catalytic activity. This consideration may be true in the case of the M(M^+) of Li^+. The relation between M(M^+) and the catalytic activity (defined by the maximum rate of reaction ($R_{\max}$)) is shown in Table 2. Table 2 indicates the marked partial electron-occupation on the vacant orbital of Li^+ in a large separation[29] at a van der Waals distance of Li-Cl (3.31 Å), even though all the M(M^+) values except M(Li^+) is almost zero. This feature of the partial electron-occupation on the vacant orbital of the cation may be related to the weak covalent nature of lithium salts, in view of the appreciable value of the overlap population (indicated by M(M–Cl)) as compared with the negligible populations of other group I metal salts. Such a weak covalency of lithium salts can be understood in terms of the very appreciable solubilities of lithium salts to organic solvents, such as alcohol and ether.

The Bond Nature of Lithium Salts. In order to investigate the nature of the bond of lithium salts, the extended Hückel molecular orbital calculation for Li_3PO_4 was carried out with the bond lengths of Li–O varying from an ionic distance (2.91 Å) to the covalent one (2.30 Å). The changes in the atomic population and the total energy with those of the distance are illustrated in Fig. 1, where the geometry used for the calculation is also portrayed. As is shown in Fig.1, the total energy of Li_3PO_4 indicates, interestingly, that the ionic structure of this phosphate is very stable. In this case, however, the total energy excludes the energies of core repulsions and electron-electron interactions. Considering the circumstances of the hydrocarbons around the metal salt-catalysts in the reaction system, it seems preferable to use the ionic structures of the catalysts. The present calculations will hereafter

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[28] In fact, phosphate, formate, *etc.* of lithium salts are more effective than halides in tetralin oxidation.[10]

[29] The bond distance of Li-Cl has been reported to be *ca.* 2.2029 Å (L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y. (1960), p. 532).

Table 2. The relation between the catalytic activity of group I metal chlorides and the electronic states of them

Compound (MCl) M	Distance of M–Cl (Å)	L.V. orbital of M$^+$	R$_{max}$ × 10^4[a] (mol/l·sec)	M (M$^+$)[b]	N(M–Cl)[c]	L. V. level of s-orbital of M (eV)
Li	3.31	2s	1.20	0.0200	0.016	−5.090
Na	3.65	3s	0.07	0.0055	0.004	−5.018
K	4.05	4s, 3d	0.10	0.0012	0.001	−4.268
Rb	4.25	5s, 4d	0.12	0.0003	0.0003	−4.164
NH_4[d]		3s	0.08			
($BeCl_2$)[d]	2.02	2p (or 2s)[e]	0.13	0.7037	0.2575	−4.338[f]
None			0.05			

a) This maximum rate was determined by the moles of O_2 absorbed corresponding to those of hydroperoxide formed in the oxidation of cumene saturated with the metal chlorides at 70°C.
b) Atomic population of the metal cation.
c) Overlap bond population between the metal cation and the anion.
d) They were taken for the purpose of comparison.
e) The L.V. orbital of $BeCl_2$ is 2p-one in the case of sp-hybrid-valence state, while that of Be^{2+} is a vacant 2s-orbital. The former may be preferable because of the feeble ionic character of $BeCl_2$.
f) This level corresponds to the vacant p-Be orbital.

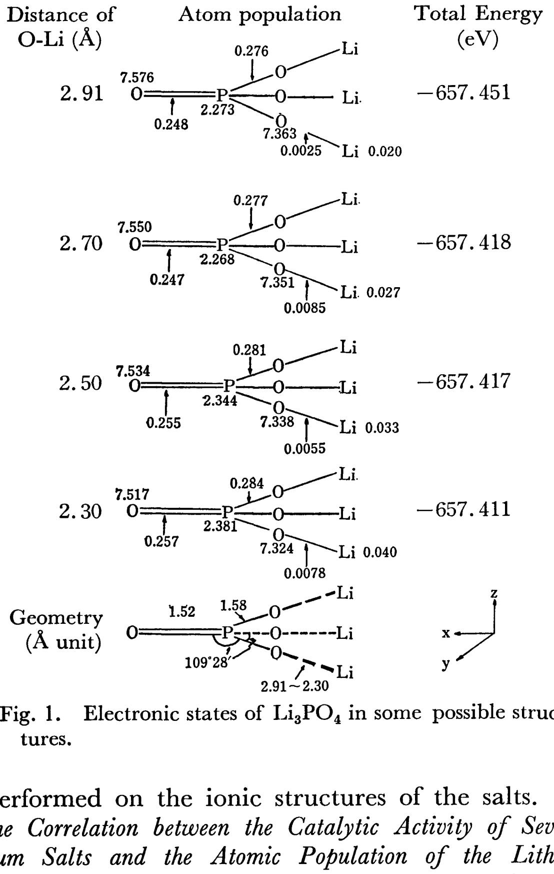

Fig. 1. Electronic states of Li_3PO_4 in some possible structures.

be performed on the ionic structures of the salts.

The Correlation between the Catalytic Activity of Several Lithium Salts and the Atomic Population of the Lithium Cation (*M*(*Li*$^+$)) *in Them.* The counter anions of salt-type catalysts appreciably affect the catalytic activity, as has been discussed previously.[7–10] It is of interest to investigate the relation between the activity (defined by R_{max}[30]) and M(Li$^+$). In this case, M(Li$^+$) would be related directly to the covalency of the bond between the lithium cation and the counter anion, as is indicated by the total overlap population of Li$^+$–X$^-$, (M(Li$^+$–X$^-$)). R_{max}, M(Li$^+$), and M(Li$^+$–X$^-$) are listed in Table 3. An interesting correlation between R_{max} and M(Li$^+$) could be found with some irregularities caused by a gap between the structures calculated and those in the reaction system. This correlation suggests that electrons on the "partially occupied" orbitals of lithium cation participate directly in the activity and that the counter anion contributes not a little toward the changing of the electron-occupation on the cation by an electron-inflow through the somewhat "covalent" bond.

Interaction between the Lithium-salt Catalysts and Molecular Oxygen. The catalytic activity of lithium salts as effective catalysts for the oxidation may be attributed to the contribution of the partially-occupied 2s-lithium orbital, in view of the above discussion. It is plausible here to discuss the interaction between the orbital mentioned above and the half occupied,doubly-degenerated 1π_g-orbitals of $^3\Sigma_g^-$ molecular oxygen, because the catalysts are unlikely to promote the reaction by the decomposition of the hydroperoxide formed, especially during the initial stage of the reaction.[10] There exist three different representative configurations of the interaction (angular-, linear-, and triangular one), as Fig. 2 indicates. Our previous report[10] demonstrated that the "angular interaction" is plausible in view of the orbital symmetry. From Fig. 2 in which the total orbital overlaps between the orbitals of Li$^+$ and 1 π_g-orbitals of O_2 are recorded, the demonstration mentioned above may be seen to be in good agreement with the present results of calculations, because the overlaps of the angular interaction is larger than those of the others. However, the strength of the interaction should vary with the direction of the orbitals of the Li$^+$ to 1π_g-orbitals of O_2; it is also affected by the total orbital overlaps between the lithium cation and the 1π_g-orbitals (S(Li$^+$–O_2(1π_g))). The variation in S(Li$^+$–O_2(1π_g)) with the angles of the interaction is shown in Table 4. Moreover, the participation of the catalyst in the electronic state of molecular oxygen accompanies the energy splitting of the 1 π_g-orbitals from the degenerated state, reflecting the Jahn-Teller

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[30] This was determined by means of the quantity of O_2 consumed to tetralin at 120°C during the formation of equimolar quantities of its hydroperoxide to those of O_2.

Table 3. Correlation between the catalytic activity of lithium salts and the atomic population of lithium cation

Catalyst	M (Li$^+$)[a]		M (Li$^+$-X$^-$)[b]		R$_{\text{max}}$[c] (mol/l·sec ×10^4)
	Method I	Method II	Method I	Method II	
LiF	−0.003		−0.008		1.98
LiCl	0.020		0.032		2.68
LiBr	0.020		0.034		2.96
LiI	0.032		0.054		0.28
$LiNO_3$	−0.012	—	−0.002	—	1.76
Li_2CO_3	0.001	0.006	0.002	0.010	1.13
Li_2SO_4	0.013	0.024	0.004	0.008	1.41
Li_2PO_4	0.008	0.020	0.0	0.006	2.05
LiOH	—	−0.001	—	−0.018	1.27
LiO_2CH	—	0.002	—	0.012	3.88
$LiO_2C_2H_5$	−0.002	—	0.0016	—	1.27
$(LiO_2C)_2$	0.0004	—	0.0008	—	1.69

a) Atomic population of Li$^+$.

b) Overlap bond population between Li$^+$ cation and X$^-$ anion.

c) These values were obtained from the data of the tetralin-oxidation catalyzed by lithium salts (2.4×10^{-2} mol/l) at 120 °C for 3.0 hr, where the moles of tetralin hydroperoxide formed corresponded to those of O_2 absorbed.

Table 4. The variation in the electronic state of O_2 with the angular interaction between LiCl and O_2

Angle of OOLi	S(Li$^+$-O$_2$·(1π_g))[a]	M (O-O)[b]		P (O-O)[c]		ΔE (1π_g)[d] (eV)	
		Method I	Method II	Method I	Method II	Method I	Method II
0°	0.007	0.476	0.460	−0.607	−0.619	0.0009	0.0010
10°	0.036	0.474	0.453	−0.607	−0.619	0.0010	0.0011
15°	0.048	—	0.730[e]	—	−0.666[e]	—	0.0014[e]
30°	0.043	0.468	0.454	−0.607	−0.619	0.0011	0.0014
60°	0.007	0.466	0.450	−0.606	−0.618	0.0006	0.0007
90°	0.036	0.464	—	−0.606	—	0.0	—
O_2 only		0.830		−0.596		0.0	

a) Total orbital overlap between the orbitals of Li$^+$ and 1π_g-ones of O_2.

b) Atomic bond population between two oxygen atoms.

c) Bond order density of the $sp\sigma$-type bond of O_2.

d) The energy difference of the 1π-orbitals removing from the degenerated state.

e) These values were obtained from the calculations by Method III.

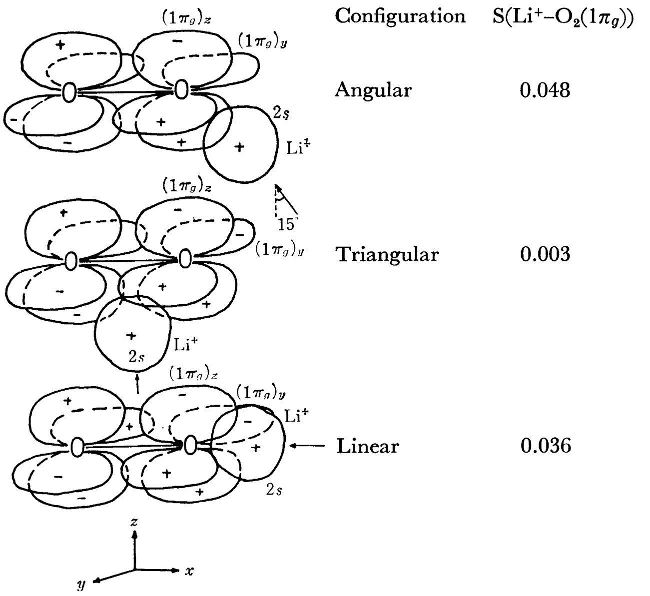

Fig. 2. Configurations of interaction between the partially occupied 2s-orbital of Li$^+$ and the half-occupied, doubly degenerated 1π-orbitals of O_2.

effect.[31,32] This situation may be understood in terms of the energy difference between the removed 1π_g-orbitals (indicated by the notation of "$\Delta E(1\pi_g)$" in Table 4). The value of $\Delta E(1\pi_g)$ suggests that the larger it becomes, the more O_2 comes to have an active radical nature.

From the data of the extended Hückel calculations by both methods (Methods I and II), shown in Table 4, S(Li$^+$-O$_2$(1π_g)) and $\Delta E(1\pi_g)$ shown clearly that the strongest interaction occurrs at the angle of 15° to the direction of 1 π_g-orbital expansion. This fact may be closely related to the bond angles of ROOH ($\angle$ROO $=105^{\circ}$[33]), H_2O ($\angle$HOH$=104^{\circ}27'$[34,35]), CH_3OH ($\angle$COH$=104^{\circ}40'$[36]), *etc.* The change in the angles of the interaction, however, has little influence upon the

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Table 5. The variation in the electronic state of O_2 with the angular interaction between LiCl and O_2

Distance of Li-O (Å)	$S(Li^+O_2\cdot(1\pi_g))^{a)}$	M (O-O)$^{b)}$ Method II	M (O-O)$^{b)}$ Method III	M (Li$^+$)$^{c)}$ Method II	M (Li$^+$)$^{c)}$ Method III	P (O-O)$^{d)}$ Method II	P (O-O)$^{d)}$ Method III	ΔE $(1\pi_g)^{e)}$ (eV) Method II	ΔE $(1\pi_g)^{e)}$ (eV) Method III	$M(O_f)$ $M(O_n)^{f)}$ Method II	$M(O_f)$ $M(O_n)^{f)}$ Method III
5	0.008	0.444	0.716	0.036	0.038	−0.628	−0.679	0.0001	0.0001	0.0005	0.0008
4	0.021	0.446	—	0.037	—	−0.626	—	0.0003	—	0.0030	—
3	0.048	0.458	0.730	0.040	0.053	−0.619	−0.666	0.0012	0.0014	0.0154	0.025
2	0.082	0.504	0.782	0.022	0.042	−0.605	−0.647	0.0017	0.0017	0.0456	0.066
1	0.059	—	0.864	—	−0.03	—	−0.654	—	0.0099	—	0.072
O_2 only		0.830				−0.596					

a), b), c), d), and e) are found in Table 2 or Table 3.

f) Difference between the atomic population of the farther oxygen atom ($M(O_f)$) and that of the neighboring atom ($M(O_n)$) for the catalyst. The former was larger than the latter.

state of the antibonding $sp\sigma$-type orbitals of the O–O bond, as is shown by the bond-order density (P(O–O)) in Table 4.

The investigation of the interaction of the lithium catalyst with molecular oxygen was, then, developed further by calculating the angular interaction with the variation in the distances of O_2-LiCl from 5 Å to 1 Å at a fixed angle of 15°. The data obtained from the calculations are summarized in Table 5. As is shown in Table 5, a monotonous increase in the total overlap, $S(Li^+-O_2(1\pi_g))$, with a shortening of the distance between the catalyst and O_2 brings about a larger separation in the orbital energies ($\Delta E(1\pi_g)$). However, in the case of the distance of 1 Å, hardly no interaction might occur because of the core repulsions of the two molecules; this is reflected by the relatively small value of $S(Li^+-O_2(1\pi_g))$. On the other hand, when the lithium catalyst interacts with O_2 at 4 Å—5 Å, the catalyst has little effect upon the activation of O_2, as is suggested by the fact that the values of $S(Li^+-O_2(1\pi_g))$ are so much smaller than those at 3 Å and 4 Å. The contour map for the interaction (at 5 Å) between the $1\pi_g$-orbitals of O_2 and the partially-occupied s-lithium orbital of the catalyst indicates little influence of the catalyst upon the orbitals of O_2, as is shown in Fig. 3. In this situation of the

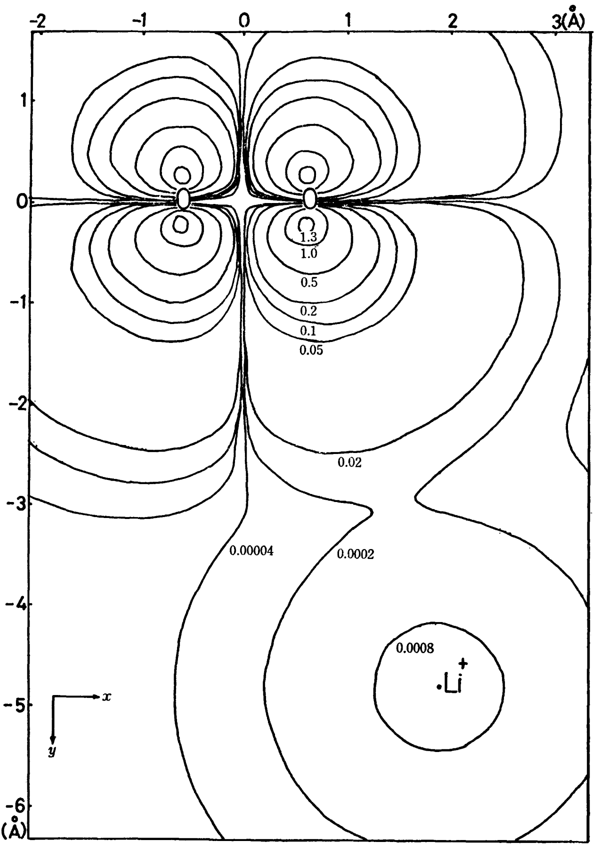

Fig. 3. Contour map for the angular interaction between the 1π-O_2 orbitals and the partially occupied s-Li orbital at 5Å. The values of the contour in this map and the following ones are those of the wave functions.

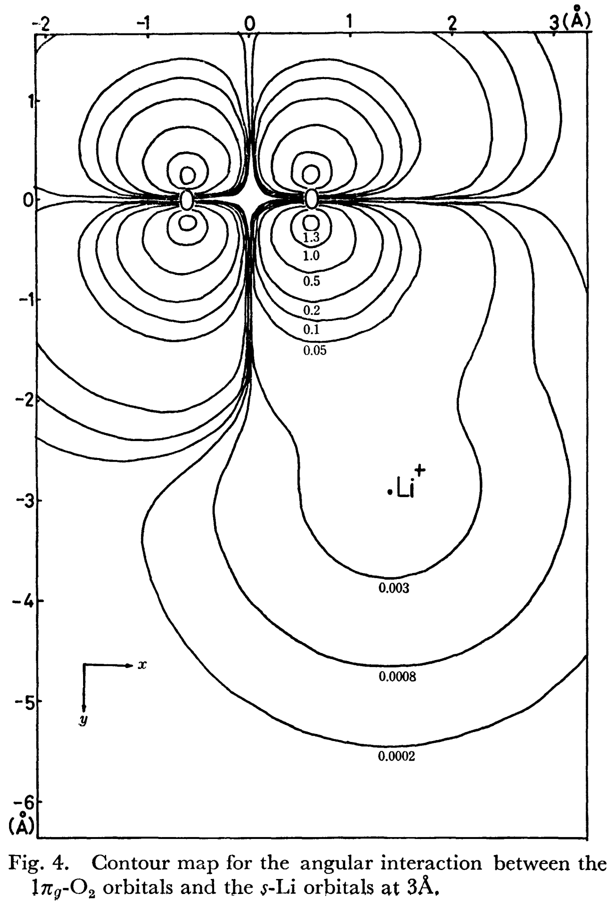

Fig. 4. Contour map for the angular interaction between the $1\pi_g$-O_2 orbitals and the s-Li orbitals at 3Å.

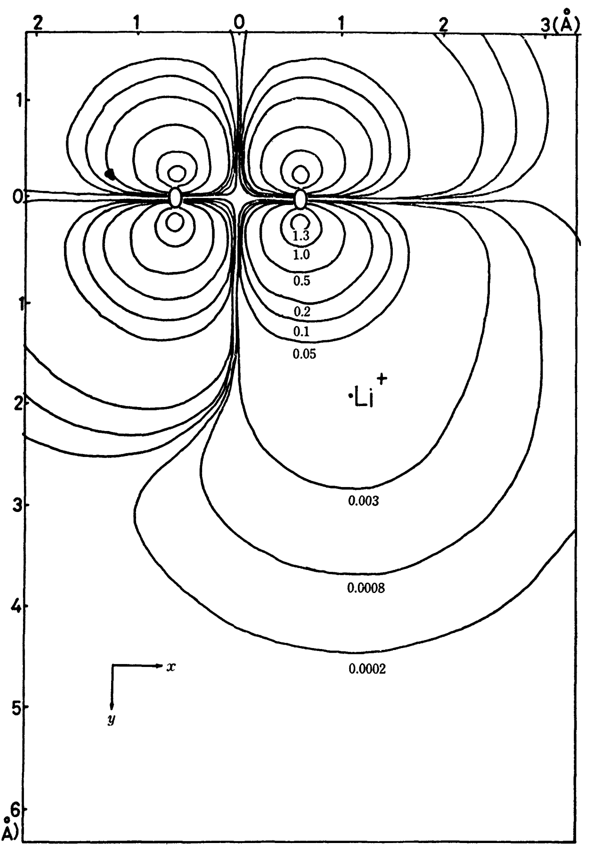

Fig. 5. Contour map for the angular interaction between the $1\pi_g$-O_2 orbitals and the s-Li orbital at 2Å.

small $S(Li^+–O_2(1\pi_g))$ value, electrons may be transferred mainly from the $1\pi_u$-orbitals of O_2 to the lithium cation to some extent, considering the increase in the atomic population of Li^+ ($M(Li^+)$) with the decrease in the distance between O_2 and the catalyst, while the total population of Cl^- stays constant. Then a favorable interaction would occur at distances from 2 Å to 3 Å, considering the $2p$-orbital expansions of O_2 and the small $2s$-orbital of Li^+. These circumstances are comprehensible in terms of the maps in Figs. 4 and 5. In this case, it is expected that electrons migrate from the partially-occupied $2s$-Li^+ orbital to the $1\pi_g$-orbitals of O_2, with a back-donation from the the $1\pi_u$-orbitals of the latter to the former. This is suggested by the decreasing $M(Li^+)$.[37]

Speaking about the population of the two oxygen atoms in O_2, the one atom remote from the catalyst, O_f, accepts more electrons than the other (O_n). Further, the $sp\sigma$-type O–O bond may lengthen its interatomic distance, since its bond-order density, P(O–O), is not only negative but also appreciably smaller than that of normal ${}^3\Sigma_g^-$ O_2 (see Table 5). Under the circumstances of hydrocarbons (RH), the position of O_f will be the more active side in O_2 for the reaction with RH: the electrons of O_f may transfer to the lowest laying, antibonding σ^*-orbital of RH through the $1\pi_g$-orbitals, thus increasing the antibonding character of the bond and causing the scission of the bond. When a hydrogen is abstracted from RH by O_2 through the cleavage of the R-H linkage, electrons migrating from O_2 to RH will be back-donated to the catalyst through the same $1\pi_g$-orbitals. Further work on the precise calculation including RH will clarify this assumption.

Finally, the results obtained from the present study may be summarized as follows:

a) Among group I metal salts, as calculated by the extened Hükel method, lithium salts were found to bear a remarkable electron-occupancy in their $2s$-orbitals; in this connection, lithium salts have a somewhat covalent bond.

b) The catalytic activity of group I metal salts can be well explained on the basis of their close relation to the atomic population of the metal cation, and the high activity of the lithium catalyst is reflected by the remarkable population of Li^+.

c) The lithium catalyst interacts most strongly with molecular oxygen at the angle of 15° to the direction of the $1\pi_g$-orbital expansions of O_2: this was understood on the basis of the suitable orbital overlap between the "partially-occupied" orbitals of Li^+ and the $1\pi_g$-orbitals of O_2.

d) Such an effect of the lithium-salt catalyst was exhibited best at the distance of 3 Å—2 Å from O_2. The electrons of Li^+ may inflow to the $1\pi_g$ of O_2 with the back-donation of $1\pi_u$ of the latter and an increase in the electron population of the farther oxygen atom (O_f) for the catalyst. This phenomenon furthered the orbital-removement of $1\pi_g$ from the degenerated state.

e) As for the hydrogen abstraction of "activated" O_2 from hydrocarbons, the orbitals of O_f take part in the abstraction more effectively than those of O_n.

The calculations were carried out on the FACOM 230.60 computer at the computation center of University of Kyushu.

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[37] The atomic population of Cl also stayed constant.